THE

THEORY OF HEAT

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PREFACE

Maqsood A. Aziz

ɔreparing this volume my object has been to treat the science eat in a comprehensive manner, so as to produce a tolerably plete account of the whole subject in its experimental as as its theoretical aspect. I have consequently enjoyed a lom in my choice of subject-matter, and mode of exposition, h would not have been possible in a work designed to meet requirements of some particular class of persons preparing xaminations or engaged in practical pursuits.

t is but a short time since the pursuit of experimental rch was regarded merely as a matter of individual curiosity; ɔwing to the high commercial value and important bearings any of the recent discoveries in the fields of science, the c mind has now become awakened to the conviction that ledge is wealth, and that the scientific education of the e is a matter of national importance.

ι the struggle for place it is not surprising that the nobler t of science, as an instrument of education and culture, l be lost sight of in the popular desire for a mere acquaint- with the facts demanded by the exigencies of the moment. ınot, however, be too soon or too often impressed upon the ıer that an acquaintance with a number of facts does not tute a scientific education, and that there is no royal road ırning other than that by which it is pursued for its ake.

e great lessons of history are not to be found in the s of battles or in the details of infamous amours and

massacres, nor in the memory of the dates, but rather in the full knowledge of the inner meaning of events, and a due appreciation of their general bearing on the social development of mankind. So also in science, that knowledge which is power is not the mere memory of facts but the comprehension of their whole meaning in the story of nature.

It is in the pursuit of this knowledge that scientific theories are formed. Without a theory all our knowledge of nature would be reduced to a mere inventory of the results of observation. Every scientific theory must be regarded as an effort of the human mind to grasp the truth, and as long as it is consistent with the facts, it forms a chain by which they are linked together and woven into harmony.

The fact that any theory, however plausible, may ultimately become untenable, demands its constant comparison with the results of experiment, and the closest scrutiny at every step of its development. In this respect, and also from an educational point of view, the historical method of treatment possesses many advantages in the exposition of any scientific subject. When this method is combined with that detail in description and explanation which is necessary to secure instruction, and also with such suggestion and criticism as may excite intellectual life and independent thought on the part of the student, it does not lend itself readily to the production of a pocket edition of the sciences. It must be remembered, however, that the most fruitful method of exposition is not necessarily that by which a given number of facts may be recorded in the smallest space, but rather that by which they may be most easily assimilated by the mind, and most comprehensively grasped in their general bearings and mutual relations; and this is the method which is most calculated to advance knowledge, and raise the intellectual character of the individual.

I have now to express my obligations to the many sources of information which I have laid under contribution during the comparatively short time allotted to the preparation of this work. Due reference is given to these throughout the text, and

t is hoped this may increase the usefulness of the book to those who desire fuller information on any particular point. I have given in detail what may be called the classical experiments of he subject, and in addition I have noticed such other investigations as will give the student a general idea of the character of the work that has been done in each department up to the present time. The diagrams with which these descriptions are llustrated have all been prepared by Mr. J. D. Cooper (188 Strand, London) with exceptional attention and despatch.

Such subjects as the steam-engine and the theory of solutions have been omitted, as they demand, and have already obtained, separate treatment in special works. The kinetic theory of gases has only been entered into so far as to meet the immediate requirements of the subject in hand; and it would be desirable to treat this, and some other subjects usually dealt with in treatises on Heat, in a separate volume.

In conclusion, I beg to offer my best thanks to Mr. Charles J. Joly, M.A., of Trinity College, Dublin, and Professor Alex. Anderson of Queen's College, Galway, for their kind assistance in reading the proofs. To Professor G. F. FitzGerald I am indebted for much valuable criticism and suggestion while the work was passing through the press, and also for the continuance of that generous assistance and advice with which he favoured me during the preparation of my work on the *Theory of Light*.

THOMAS PRESTON.

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CHAPTER I

PRELIMINARY SKETCH

SECTION I

INTRODUCTORY

1. THERE is, perhaps, no scientific inquiry more full of human interest, than the study of the nature of heat, and the manner in which matter in general is affected by it. No branch of physical science is so intimately connected with the everyday occupations of life, and, consequently, none of them interests mankind more closely.

The influence of heat is manifestly so universal, and its actions so important and necessary to the progress of all the operations of nature, that, to those who first considered it with some attention, it must have at once appeared to be the general principle of all life and activity on this globe. With its return in springtime the bud breaks into blossom, and new life animates the vegetable kingdom. By its agency the incubation of the egg progresses, a living thing is brought into the world, and heat is still necessary to its support. Finally, to the power which man has acquired over it is due that supernatural strength which has made him superior to all other animals, and master of land and sea.

It is not surprising, therefore, that an agent at once so powerful and so serviceable, so beneficent, and yet sometimes so terrible, should have become a subject of adoration and worship among the inhabitants of the earth, but at first sight it may seem more than surprising that its study in early times should have been so much neglected.

2. This indifference can only be attributed to that lack of attention with which men always regard those things which they are accustomed to use instinctively for their needs, and which they have before them at all times. The first instinct of man is to direct and use the forces of nature for the purposes of life. Theorising follows afterwards. The early acquisition of this practical knowledge is proved by mighty monuments which were raised by the workmen of the earliest historic times. The magnificent temples of India, the

vast pyramids of Egypt, the noble architecture and sculpture of Greece and Rome, prove that the engineers of those days had acquired a knowledge of some of the methods of transporting cyclopean masses. Various hydraulic and pneumatic apparatus were certainly in vogue, and many engines were invented by Ctesibus and his pupil Hero.

The ancient philosophers were, however, strongly disinclined to impart their learning to the public, and each in general communicated it only to his special disciples. They all esteemed it an essential part of learning to be able to conceal their knowledge from the uninitiated, and even those who were most celebrated for their inventions were so infected by this superstition that they refrained from leaving any written account of their discoveries,—a practice which was certainly detrimental to the advancement of posterity.

3. The question, "What is heat?" must, however, have been proposed and pondered over by all inquiring minds from the earliest times. Man could not go on for ever using fire to cook his food and warm his body without seeking to know something of the source and nature of this agent. The inquiring mind cannot rest satisfied with the mere observation of the facts of nature, but is irresistibly led to investigate their origin and cause. The fact of highest interest and importance is that the sun illuminates and warms the earth, and the questions which must have presented themselves earliest to the attention of philosophers were, "What is light?" and "What is heat?" A question of a much simpler order is, "What is sound?" and that any satisfactory answer has been obtained to the two former is probably owing to the proposition and solution of the latter. Amid the phenomena of sound we deal with a medium which we can subject to experiment, and whose properties we can thoroughly examine, but in the phenomena of heat and light we step at once into the sanctuary of the unknown. From the domain of the visible and tangible we pass into that of the invisible and intangible. The known process, however, gives direction to the line of thought, and, reasoning by analogy, the imagination expands from the domains of the senses and embraces in thought the regions which lie beyond it. By observation and experiment the human mind becomes acquainted with a knowledge of the properties and relations of things, and, reasoning upon the information thus supplied, we rise to the explanation of the unknown and intangible by means of the ideas which we have gained from what is known and tangible.

The reverse and less philosophic process—the explanation of the visible by means of the invisible—seems to have been the general habit of those who first speculated in physical science. In all the

pursuits which required refined taste and the native powers of the intellect, the ancient Greeks were pre-eminent. They possessed, as if instinctively, the perception of everything that is sublime and beautiful. They were keen observers of men, but as physical philosophers they failed, not perhaps from want of genius or application, but because they pursued a false path; because they reasoned more upon an imaginary system of nature than upon an accurate knowledge of the facts; and tried to explain physical phenomena by resorting to speculation more than to observation and experiment. The general tendency was to explain the seen by means of the unseen, and to appeal to the imagination rather than to observe facts. Thus, the general effects of heat were *explained* by the invention of *fire atoms*, which drove furiously through the pores of bodies, and loosened their molecules asunder, reducing solids to liquids, and liquids to vapours.

4. The systematic study of heat, as a distinct branch of experimental science, commenced little more than half a century ago. Previously the nature and effects of heat (or fire) were investigated only by the chemist, whose most powerful agent and ally it has always proved. One of the earliest attempts at theorising in chemistry originated in the explanation of the nature of combustion, and, consequently, in tracing the origin and growth of our subject we are led back to the early study and growth of the science of chemistry, and of experimental inquiry in general.

Although the practice of alchemy seems to have been common among the Egyptians in very remote ages, yet the origin of experimental inquiry cannot be dated farther back than the seventh or eighth century of the Christian era. Its inception seems to have been coeval with the short period during which cultivation and scientific learning were promoted by the Arabians. Actuated by the desire for wealth, the alchemists ardently prosecuted the search after the artificial production of the noble metals, and visionary as may have been their hopes, yet they made experiments, and the experiments of the alchemists were more calculated to extend the bounds of human knowledge than the speculations of the Greeks.

While Greece and Italy sank into barbarism, the early Mohammedans, who had previously destroyed almost all the records of the progress of the human mind, rekindled the light of learning, and became the cultivators of a new science. From Egypt, where they became acquainted with the Aristotelian philosophy and chemistry, they penetrated through northern Africa, and crossed over into Spain, and here arts and sciences flourished under their dominion. The academies of Spain were soon thronged with students from all parts

of the Christian world, the knowledge of alchemy spread, and in the thirteenth century alchemists of the Arabian school were established in all the chief countries of Europe.

5. Amongst a people of conquerors disposed to sensuality and luxury, even from the very spirit of their religion, and who were romantic and magnificent in their views of power, it was not to be expected that any new science would be pursued in a rational and philosophic manner. As a consequence the early discoveries in chemistry led to the practice of alchemy, the objects of which were to produce a substance (*the philosopher's stone*) capable of converting all the other metals into gold, and to discover *the elixir of life*—a universal remedy against old age, calculated to preserve youth and prolong indefinitely the period of human life.

The processes relating to the discovery of the philosopher's stone and the elixir of life were probably widely diffused by means of the Crusades, for many of the warriors who, animated with visionary plans of conquest, fought the battles of their religion in Palestine, seemed to have returned to their native lands under the influence of a new delusion.

At this time the public spirit of the West was calculated to assist the progress of all pursuits that carried with them the air of mysticism. Burning with the ardour of a rapidly-extending and exalted religion, men were much more disposed to believe than to reason. In all times, however, the love of knowledge and power has been instinctive to the human mind; in darkness it desires light, and follows it with ardent enthusiasm, even when appearing in delusive glimmerings.

6. The middle ages consequently constitute what may be regarded as the heroic, or fabulous, epoch in experimental physics, and, as might be expected, their records contain a great variety of anecdotes relating to the transmutation of metals, and the views or pretensions of persons considered as adepts in alchemy.

Some of these alchemists were low impostors, whose object was to delude and defraud the credulous and ignorant. Others seem to have deceived themselves with vain hopes, but all followed the pursuit as a secret and mysterious study. The processes were communicated only to a few chosen disciples, and, being veiled in the most obscure and enigmatic language, their importance was enhanced by their ambiguity.

In all ages men have been governed more by what they desire or fear than by what they know, and in this age it was particularly easy to deceive, but difficult to enlighten, the public mind.[1] Truths, how-

[1] That the delusions of alchemy were ardently pursued may be learned from the public acts of these times. In 1316 the alchemists were openly condemned by Pope

ever, were discovered, but they were so blended with the false and marvellous that another era was required to separate them from concomitant absurdity, and to demonstrate their true importance and uses.

The alchemists in chemistry have been somewhat like the perpetual motionists in natural philosophy. Both, by seeking after the impossible, have led up to discoveries of the greatest importance and practical value. Both, like the fabled husbandmen of old, by seeking after brilliant impossibilities, sometimes discovered useful realities.

7. Even in these times, however, progress was made, and there were some who essayed to form scientific views. Men of exceptional intellectual power were found differentiating themselves from the crowd, and seeking to connect natural phenomena with their physical principles. By the early alchemists the elements had been placed under the dominion of spiritual beings, and their followers in Europe conceived gnomes and nymphs, sylphs and salamanders, genii and fairies, capable of being governed and enslaved by man. These spiritual agents seem to have originated with the alchemists, who all professed to believe in supernatural powers, in an art above experiment, and a system of knowledge not derived from the senses. In addition, the systems of logic, adopted in the schools, were founded rather upon the analogies of words than upon the relations of things, and they were consequently more calculated to conceal error than to discover the truth.

8. With the revival of literature in Europe came the desire for philosophic discussion in the sciences. The diffusion of letters gradually brought the opinions of men to the standard of truth and nature. Failures in the experimental arts produced caution, and the frequent detection of imposture created rational scepticism. Science demanded the extirpation of the gods and demons which haunted its domains, and called for absolute reliance upon law in nature. The supernatural was swept from the field, and gave place to a rational basis for natural phenomena, and the problems previously attacked from above were now approached from below.

In the beginning of the thirteenth century Roger Bacon of Oxford applied himself to observation and experiment with characteristic talent and sagacity. A man of truly philosophic turn, desirous of investigating nature, and of extending the resources of art, his

John XXII. as impostors, who promised what they did not perform, and in England an Act of Parliament was passed in the fifth year of the reign of Henry IV., prohibiting attempts at transmutation, and rendering them felonious.

inquiries offered some very extraordinary combinations, but neither his labours nor those of Albert of Cologne (a contemporary genius of kindred spirit) seem to have had any considerable influence on the improvement of his age. The wonders performed by the experimental art were attributed by the vulgar to magic, and at a time when knowledge resided only in the cloister any new philosophy was regarded by the learned with a jealous eye.

9. Till the time of Lord Bacon there had been no distinct views concerning the art of experimental inquiry. It was left for him to point out how little could be effected by the unassisted human powers. He directed the attention of inquirers to artificial resources and the use of instruments for assisting the senses, and for examining bodies under new relations. He taught that man was but the servant and interpreter of nature, capable of discovering truth in no way but by observing and imitating her operations; that facts were to be collected before speculations were formed; and that the materials for the foundations of true systems of knowledge were not to be discovered in the books of the ancients, nor in metaphysical theories, nor in the fancies of men, but by observation of the visible and tangible in the external world.

Facts are independent of taste and fashion, and are subject to no code of criticism. They are perhaps more useful when they contradict than when they support received doctrines, for our theories at best are only imperfect approximations to the real knowledge of things, and in all physical research doubt is usually an incentive to new labours, and tends continually to the development of truth. The thoughts and questionings of man turn towards the sources of natural phenomena and seek a knowledge of the actions which underlie them. By a process of abstraction from experience physical theories are formed which lie outside the pale of experience, but which satisfy the desire of the mind to see every event in nature resting upon a cause. Natural philosophy is an *experimental* and not an *intuitive* science, and *a priori* reasoning cannot alone conduct us to a physical truth. We must endeavour to discover what it is, and not speculate on what it might be, or decide on what ought to have been, and the causes and connections of the phenomena of nature have escaped the apprehension of man for ages by the wilful ignoring of this fact.[1]

10. About the middle of the seventeenth century mathematical and physical investigations were pursued in every part of the civilised world with an enthusiasm before unknown. The new mode of

[1] See Tait's *Sketch of Thermodynamics*. Edinburgh: David Douglas.

improving knowledge by collecting facts, associated together a number of labourers in the same pursuit. It was felt that the whole of nature was yet to be investigated, and that there were distinct subjects connected with utility and glory, sufficient to employ all inquirers, yet tending to the common end of promoting the progress of the human mind.

Learned bodies were formed in Italy, England, and France, for the purpose of the interchange of opinions, the combination of labour, the division of expense in performing new experiments, and the accumulation and diffusion of knowledge. The Academy del Cimento was established in 1651, under the patronage of the Duke of Tuscany; the Royal Society of London in 1660; and the Royal Academy of Sciences of Paris in 1666. A number of celebrated men, who have been the great luminaries of the different departments of science, were brought together or formed in these noble establishments. The ardour of scientific investigation was excited and kept alive by sympathy. Taste was improved by discussion, and by a comparison of opinions. The conviction that useful discoveries would be appreciated and rewarded was a constant stimulus to industry, and every field of inquiry was open to the free and unbiassed exercise of the powers of genius.

11. Chemistry had scarcely begun to assume the form of a science when the attention of all the most brilliant intellects became directed to another object of research. The Newtonian philosophy sprang into full life at a single bound, and its objects were calculated by their grandeur to monopolise the attention of the most gifted men of the age. The effect occasioned on the scientific minds of the time has been compared to that which the new sensations of vision produce on the blind receiving sight. The highest interest and most enthusiastic admiration were awakened, and for nearly half a century the new study engrossed the thoughts of the most eminent philosophers of Europe.

At length the current of scientific thought began to flow in other channels, and in the latter half of the eighteenth century the foundations of a systematic inquiry into the nature of heat were laid by Black, Wilcke, Crawford, Irvine, and Lavoisier, followed by Rumford, Pictet, Herschel, Leslie, Dalton, Davy, Gay-Lussac, and many others. On the basis thus firmly laid a noble edifice has since been raised, a lasting monument to the genius of the nineteenth century; and from base to highest battlement may be traced the work of our illustrious countrymen—Rankine, Joule, and Thomson.

12. A review of the opinions of the ancients, and of their specula-

tions in physical science, may prove amusing in some parts, but everywhere it is a most instructive task. Their writings on every branch partake more of the character of a record of ingenious speculation than of experimental inquiry. Hypotheses of a mystical character were framed to explain the phenomena of nature, and physical results were based on meaningless dogmas. Men were told that the planets move in circles *because* circular motion is perfect, and systems of physics were founded on the assertion that "nature abhors a vacuum" and the Latin dogma, "causa equat effectum." While this lasted progress in the physical sciences was impossible. Dogma was handed down from generation to generation, and free thought found no place in the schools of the middle ages.

It is, however, unfair to boast of the progress of the nineteenth century as compared with that of the generations which have preceded it. At a time when little is known men grope after knowledge in the dark, and though the gateway may be near at hand, the entrance may not be effected, until happily some one stumbles in by accident. Once entered, the passage becomes easy for those who follow, and future progress is enormously assisted by the history of the failures and successes of those who have gone before. Difference of native intellectual power in different ages is not so much the cause of the varying success attending the labours of men as the peculiar nature of the artificial resources and means in their possession. At all times progress is retarded by absolute reliance on the work of great masters. The first function of the human mind is to doubt, and to free itself from prejudice and from all testimony which may deceive the senses. Emancipation from the slavery of superstition and the influences of early education is a very slow process. Sentiment is constitutional to mankind, and the strongest intellects find it hard to break away from the teaching of those whom they have early learned to reverence, even when its errors are clearly and conclusively pointed out to them. Throughout this long period the spirit of free inquiry was growing and gathering strength for a brave struggle against the superstition and mysticism in which it was entangled. The germ of true scientific inquiry finally took root and flourished. Intellectual health ensued, and resulted in scientific progress. The abominations of the alchemists were swept away, the spirits of the air disappeared, and the pursuit of science became the free inquiry after truth.

The history of such a period is therefore not merely a matter of curiosity. It is a great lesson to all subsequent ages. It shows that truth in physical science is not to be sought for in dogma, nor can a system of nature be built up from our inner consciousness, but that it

must be sought for earnestly and honestly by patient observation and skilled experiment.

It is sometimes asserted that metaphysical speculation is a thing of the past, and that physical science has extirpated it. But as long as the mind of man is fresh, speculation will continue as fascinating as it was in the days of Thales. Perhaps at no time has the scientific atmosphere been more pregnant with speculation than at present. Almost every day fresh discoveries are made and new theories formulated and advanced on doubtful or entirely hypothetical foundations. At the same time the germs of all kinds of mental disorders are rife. Perpetual motionists and believers that the earth is flat have not yet become extinct. Spiritualists and quack scientists increase at an amazing pace, and the patent-medicine man grows wealthy, while the spirit of true scientific inquiry sickens in the fierce struggle for existence.

SECTION II

PRELIMINARY REMARKS ON THE GENERAL EFFECTS OF HEAT, AND ON THE MEANING OF THE TERMS USED IN THE SUBJECT

13. **The Sense of Heat.**—The terms hot and cold are primitive words of the language referring to a certain class of sensations which we experience through the *sense of heat.* The sense of touch is regarded by some as a double sense, embracing that of heat as well as that of force or resistance. When a body is touched with the hand two very distinct sensations are in general experienced, one a feeling of resistance or force, and the other of warmth or coldness derived through what is termed our sense of heat. The latter class of sensation is also experienced when we sit in the sun or before the fire, or in the neighbourhood of any hot body, and consequently to excite it actual contact with matter is not necessary. It is therefore not at all obvious that the sense of heat is part of, or in any way related to, the sense of touch. On the contrary, it appears to be much more closely related to the sense of sight. A hot body is to be regarded as the source of an influence which affects the sense of heat just as a luminous body is regarded as the source of an influence affecting the sense of sight. The name given to the active agent in the former case is *heat* and in the latter *light*, and we shall see as the subject progresses that these two influences are of the same character, and that the nature of the active agent in one case is the same as in the other. The sense of heat, therefore, is quite as distinct as the sense of sight, and is certainly less related to the sense of touch than is the sense of taste or smell, which both depend upon contact with some form of matter (see further, p. 33).

14. **Definition of Temperature.**—The words hot and cold, or hotness and coldness, refer to the state of a body as judged by the sense of heat. By means of this sense we say that one body is hot and that another is cold, or that one body is hotter than another. If several pieces of the *same* substance be given, we can by means of the sense of

heat alone arrange them in order so that each shall be hotter than all that precede it in the series and colder than all that come after. We are hence led to the idea of a *scale of hotness*, and to inquire how much one body is hotter than another.

The estimation of the hotness of a body must of course be relative to some scale or standard of measurement. When this standard is chosen we may speak scientifically of the hotness of a body, and for this purpose the word *temperature* is employed. The word temperature thus means simply the degree of hotness of a body measured according to some arbitrarily chosen scale. It is a *scientific* term, and contains all the meaning of the primitive word hotness, as well as the idea of a measure of the hotness. It embraces two conceptions—first, the idea of equality of hotness, or that condition of two pieces of matter when they are said to have the same temperature; and secondly, the idea of difference of hotness and of its mode of measurement. Scientific term.

By means of the sense of heat alone a series of pieces of the *same* substance might be arranged in order of temperature, or the equality of temperature of two pieces of the same substance might be fairly accurately judged, and if the impressions could be distinctly remembered a system of measurement of temperature might be founded on the sense of heat alone. Accuracy by this method would be practically impossible, for the recollection of even a single temperature can be only roughly retained by those who specially cultivate the sense of heat for this purpose, such as bath attendants or hospital nurses. For scientific purposes it is therefore highly desirable to estimate temperature by some property of matter which varies continuously with the hotness, and which always remains the same at the same hotness.

Intervals of hotness cannot, however, be *measured* in the proper sense of the word. They may be indicated in a thoroughly definite manner, according to some chosen scale or standard, but one hotness cannot be expressed in terms of another in the same sense that one length or mass may be expressed in terms of another. In order to *measure* any magnitude we must compare it with some other magnitude of the same order which is taken as the unit. Thus a measuring tape is constructed by adding together any number of units of length, but we possess no means of adding together in the same way units of hotness. When, however, the scale of temperature is laid down and graduated by arbitrary definition, then the interval between two consecutive divisions may be said to be equal to the interval between another pair, just in the same sense as the distance between any consecutive pair of divisions on a scale of length is said to be equal to that between any other pair.

15. Expansion.—One of the most general effects of change of temperature or hotness in any body is change of bulk, or expansion by heat. The bulk of every body, with few exceptions, is found to increase continuously with its hotness, and consequently this change has been selected as the basis of a method of measuring temperature. The mode by which the change of temperature is indicated by the change of volume of course remains a matter of choice, as well as the particular substance employed.

General effects.

There are many ways of exhibiting the expansion of solids by heat, and several of these are so common that almost every one must be familiar with them. Thus the metal rails on a railway track are laid not with their ends in contact, but with a short space between to allow for expansion in summer, and for the same reason in large structures, such as metal bridges, the beams are not fixed rigidly at both ends, but a certain play is allowed so that they may expand without warping or rupturing the structure. This expansion is also made use of in the shoeing of cart wheels, the tire being slipped on while hot, and as it cools it contracts and clasps the wooden frame within. A similar application occurs in the bracing together of the walls of a building which suffer from an outward lean. Strong bars of iron are thrust through the building and secured on the outside while hot, and on cooling the bars contract and pull the walls together. To expansion also is to be attributed the ventilation of mines and houses, as well as the general circulation of water and air on the earth's surface, and the effect of these great ocean streams and air currents is to produce a more uniform distribution of temperature.

A familiar class illustration is that known as Gravesande's ring. A metal sphere which just passes through a ring when cool, when heated over a lamp will no longer pass through. Its diameter is now larger than that of the ring, but in cooling it contracts and again passes freely through. In the same manner a metal bar which fits into a tube when cold cannot when heated be passed into the same tube. It is for this reason, that a glass stopper tightly jammed in the neck of a bottle may be easily removed by heating the neck. The heat of the hand placed around the neck of the bottle is often sufficient for this purpose. If the stopper happens to be colder than the neck of the bottle when it is inserted in it, then, as the neck cools, it contracts and grasps the stopper tightly. In the same manner ordinary tumblers often become wedged within one another, and in such cases, if the inner is initially much colder than the outer, the contraction of the latter or expansion of the former may lead to the fracture of one or both.

One of the most interesting illustrations of expansion, however, is presented in the gradual creeping of a sheet of metal down a slope. Take the case of a long bar of metal lying lengthwise down an inclined plane. When the temperature increases the bar expands and pushes forward its lower end rather than its upper, on account of the action of gravity which facilitates motion down the plane rather than up it. In the same way, when the bar cools it contracts and draws in its upper end, and this process goes on with every variation of temperature, the result being that the bar gradually creeps down the incline worm-wise by alternately pushing forward its lower, and pulling in its upper end. The gradual creeping in this manner of the sheet lead covering the choir of Bristol Cathedral is cited by Professor Tyndall,[1] the rate of motion being about 9 inches per annum.

Similarly, by placing a metal bar on wheels capable of rotation in one direction only, the system will creep forward in this direction with every variation of temperature, so that the ordinary variations of temperature by day and night will cause this apparatus to move in any desired direction, up hill or down, and during this motion it might be loaded in any way, and perform the part of a heat engine. The motion, of course, would be very slow unless special means were devised to increase it. Thus, for example, the bar might be replaced by a highly expansive liquid enclosed in a large bulb furnished with a cylindrical tube in which a piston is fitted. When the temperature rises, the liquid in the bulb will expand and push the piston forward, and when the temperature falls, the liquid will contract, leaving a vacuum behind the piston, and for this reason the bulb will move forward, since on account of the construction of the wheels on which the instrument is supported the piston cannot move back. Similar apparatus may be constructed by supporting on wheels bent tubes filled with some expansive liquid or a bent strip of two or more metals welded together, such as those employed in metallic thermometers (see Art. 93). In principle, however, all such forms of apparatus are the same as the curiosity known as Stevenson's Creeper.[2] Creepers.

In the case of solids, the volume may be measured directly, and the absolute expansion determined, but in the case of liquids, which must be enclosed in some solid envelope, the expansion of the liquid is complicated by that of the vessel which contains it, and the result observed is the relative or apparent expansion of the liquid in the envelope. Thus, for example, if a large bulb furnished with a narrow Apparent expansion.

[1] Tyndall, *Heat a Mode of Motion*, p. 95, 6th edition.
[2] Described in Tait's *Heat*, p. 116.

stem, or a flask with a narrow neck, be filled with a liquid, and then heated over a lamp, the liquid will at first be observed to descend in the neck as if it contracted when heated. Soon, however, the apparent contraction ceases, and the liquid begins to rise in the stem, and continues to do so as the temperature becomes more and more elevated. The first effect is due to the sudden expansion of the flask before the general mass of the liquid becomes warm. For this reason the internal volume of the flask is increased while the volume of the liquid is scarcely altered. Soon, however, the liquid grows warm and expands accordingly. If the expansion of the liquid be greater than that of the envelope, the level of the liquid will rise in the neck, but if it be less, the level of the liquid will fall. The level would neither rise nor fall if the expansion of the liquid were the same as that of the envelope. The movement of the liquid in the stem, therefore, does not indicate its absolute expansion, but only its apparent expansion, or its expansion relative to that of the material of the envelope.

16. Change of State.—Another general effect of heat on matter is change of physical state. By sufficiently increasing the temperature, solids are converted into liquids, and liquids into vapours. While either change is taking place the temperature of the mass is found to remain constant till the change is completely effected. Thus, if a vessel full of broken ice be placed over a lamp, the ice will gradually melt, but the temperature of the whole mass will not alter till the melting is completed. The heat received is employed in changing the state of the substance, in converting it from solid ice to liquid water. If the supply of heat be still continued, the liquid will rise in temperature and ultimately begin to boil. When this point is reached, the temperature again remains stationary. The liquid simply passes into vapour, and the heat supplied during this process is used up in changing the state of the substance from that of liquid to that of vapour.

The change of physical state of any substance thus furnishes us with two fixed temperatures when the conditions under which the change takes place are given. Such changes are often very abrupt, and are consequently not suited to the estimation of temperatures which vary continuously or rapidly. They serve rather to indicate particular temperatures. For this reason the property made use of most commonly in practice is the change of volume of some liquid contained in a glass envelope, such as the ordinary mercurial thermometer.

17. The Mercury Thermometer.—For the better understanding of the subsequent matter of this chapter, it may be well to briefly

describe here the ordinary mercury thermometer,[1] which is the instrument most commonly employed in the measurement of temperature. The property made use of in this instrument for the measurement of temperature is the expansion of mercury enclosed in a glass measuring flask, or volume indicator. This consists of a glass bulb, generally cylindrical or spherical, furnished with a stem of capillary bore (Fig. 1). The bulb and part of the stem are filled with mercury, and, as already explained, the level of the mercury in the stem will vary with the temperature, unless the glass and the mercury expand equally when heated. As a matter of fact, the mercury is much more expansive than the glass, and the level of the mercury rises in the stem as the instrument grows warmer.

Fig. 1.

Here, then, we have an instrument, the indications of which vary continuously with its hotness, and which will always show the same indications under the same conditions, and which, therefore, supplies a mode of measuring temperature, and enables us to define degrees of temperature, so that it shall in some way indicate the hotness of a body, and thus replace our sense of heat.

In order to obtain a numerical measure of temperature the instrument must be graduated, and for this purpose two fixed temperatures are chosen. The points of the stem at which the mercury stands at these two temperatures are marked, and the portion of the stem between them is divided into any desirable number of parts of equal capacity. The two fixed points correspond to the temperature of melting ice and the temperature of the vapour of water boiling under the pressure of a standard atmosphere, it having been found that when the instrument is placed in melting ice, or snow, the mercury always stands at the same point, and this, according to our chosen measure, means that ice always melts at the same temperature under the atmospheric pressure, and for the same reason the steam of boiling water is used to determine the second fixed point.

We have now a perfectly definite standard of reference for all other temperatures. For example, if the mercury stands below the lower fixed point, then we say that the temperature is below the freezing point of water, or what is the same thing, the melting point of ice, and if it stands above the upper fixed point we say the temperature is higher than the boiling point of water under the pressure of one atmosphere, while for intermediate points we have

[1] The general subject of Thermometry is considered in Chap. II.

intermediate temperatures. In order to refer to these temperatures conveniently, the interval between the two fixed points on the stem is divided into a number of equal parts. Let us suppose that it is divided after the manner of Celsius into 100 parts, the lower fixed point reading 0° and the upper 100°; and let the same process of division be continued on the stem above the upper and below the lower fixed point. Then if the mercury stands at 20°, we refer to this as the temperature 20°, meaning thereby that the temperature is such that when the thermometer attains it, the mercury stands in the stem at the division 20°. We do not imply, however, that when the mercury stands at 40°, the temperature is twice as high (in the sense of the hotness being twice as intense) as when the mercury stands at 20°, or that when it stands at 100°, it is four times as hot as when it stands at 25°. It is only in this sense that we have said we cannot *measure* hotness. The thermometer is an indicator which enables us to determine equality of temperatures, and tells us how much one body is hotter or colder than another, in terms of our chosen scale. It indicates degrees of hotness, and ought always to show the same reading when at the same hotness. By making the bore of the stem very fine and the bulb large, the instrument can be rendered very sensitive, so that small changes of temperature which would otherwise escape notice can be registered.

In this method of estimating temperature some particular substance is chosen, and then by definition the change of temperature is taken proportional to the change of volume of the thermometric substance, or rather to the change in the reading of the thermometer. Once a substance is chosen, and a thermometer constructed, this may be regarded as the standard instrument by means of which all others can be standardised, so that all thermometers will agree in their indications. If this plan were adopted, we would be furnished with a definite and consistent method of estimating temperature. All thermometers would be copies of a standard instrument, just as our weights and measures are copies of arbitrarily-chosen originals, kept for the sake of reference. This plan, however, as will be seen afterwards, is not absolutely necessary, for instruments can be constructed which will agree sufficiently well in their indications without previous comparison. Such agreement is not found, however, among instruments which are not constructed of the same materials. Thus a mercury thermometer, although it agrees with an alcohol thermometer at the fixed points 0° and 100°, will in general disagree with it at the other parts of the scale. Some standard of comparison must therefore be chosen, by means of which all

Standard instrument.

thermometers are to be graduated, and for this purpose the air thermometer possesses special advantages (see Chap. II.).

18. Expansion of the Thermometric Substance — Coefficient of Expansion.—We shall now consider the relation between the volume and temperature of the thermometric substance, that is, the substance by the expansion of which temperature is measured. This relation is determined entirely by the method chosen for measuring temperature, and is not to be regarded as a new result connecting volume and temperature.

Let it be supposed that equal changes of temperature are measured by equal changes of volume of some substance. Then if V_0 be the volume at the zero of the scale, and V the volume at any temperature θ, we have—

$$V - V_0 = v\theta,$$

where v is the increase of volume for one degree, or what may be called a degree measure, and is by definition the same all along the scale. This formula is merely the algebraic method of stating the definition, or the mode of measuring temperature, and may be written in the form—

$$V = V_0\left(1 + \frac{v}{V_0}\theta\right) = V_0(1 + \alpha\theta).$$

The quantity $\alpha = v/V_0$ is obviously the expansion per unit volume of the substance in changing its temperature from 0° to 1°. This quantity is called its *coefficient of expansion* at zero. In general, the coefficient of expansion of a substance is measured by the change in bulk of a unit volume of the substance per degree of temperature. If V and V′ denote the volumes at temperatures θ and θ' respectively, then the change in bulk of a unit volume is—

$$\frac{V' - V}{V},$$

and the average change in bulk per degree of temperature between θ and θ' will be—

$$\frac{V - V'}{V(\theta - \theta')}.$$

This is termed the *mean coefficient of expansion* between the temperatures θ and θ'. In the case of the thermometric substance, the mean coefficient of expansion between zero and any temperature θ is constant and equal to v/V_0, for we have by definition

$$\alpha = \frac{v}{V_0} = \frac{V - V_0}{V_0\theta}.$$

It is to be carefully observed that this formula holds only for the thermometric substance, and follows for it as a result of our definition of temperature, whereby equal increments of temperature are measured by equal absolute increments of volume of this substance. In the case of the thermometer just described the expansion of the mercury is measured by the rise of the column in a capillary glass tube. The expansion thus observed is not the *absolute* expansion of the mercury, but only its *apparent* expansion in a glass envelope. If the stem is originally divided into parts of equal capacity, these will increase as the temperature rises, owing to the expansion of the glass. Hence, if temperature is measured by the absolute expansion of mercury the expansion of the glass must be taken into account in graduating the stem of a thermometer. Correction in this respect will render the degree intervals shorter and shorter as we proceed up the scale. If the divisions were to be equidistant along the stem its bore would have to be conical, or the substance of the envelope would require to be non-expansive. It follows, then, that if a denotes the zero coefficient of absolute expansion of the thermometric substance, the foregoing formula applies only to that substance. In the case of any other substance the volume at any temperature $\theta°$ will be some complicated function of the temperature, and we may assume that it can be expressed in the form—

$$V = V_0(1 + a\theta + b\theta^2 + c\theta^3 + \ldots),$$

where V_0 is the volume at zero.

19. Temperature Equilibrium.—If, when a thermometer is placed in contact with several bodies, or dipped into different liquids, it shows the same reading in each case, we say that all these substances are at the same temperature. If now any pair of these substances be placed in contact, or mixed together, it is found by experiment that they still continue at the same temperature (provided no chemical action occurs). It is thus found that when there is equality of temperature before contact (or mixture), this equality remains after contact. In this case there is said to be equilibrium of temperature, and we are furnished with the *experimental fact* that bodies which are in temperature equilibrium with the same body are also in temperature equilibrium with each other.

If, however, two bodies at different temperatures are placed in contact it is found that in general the temperature of the warmer falls while that of the colder rises, and this process continues till equilibrium is established. There are cases, however, in which the temperature of one changes while that of the other remains fixed.

This process takes place when one of the bodies is changing state, as when a mass of ice is placed in a basin of hot water. Here the ice gradually melts, but its temperature remains the same, while that of the water gradually falls, till the melting is completed, or equality of temperature is established. A similar process occurs when a liquid is being converted into vapour.

20. Quantity of Heat.—In order to account for the sensation experienced in presence of a hot body an active agent is postulated, and the name given to this agent is heat. A hot body is regarded as the source of heat just as a luminous body is regarded as a source of light. In the same way, when two bodies at different temperatures are placed in contact, the temperature of the warmer falls while that of the other rises. To account for this we say that *heat* passes from one to the other, that the warmer loses heat and the colder gains it. In this sense heat is regarded as something which may be added to or taken away from matter; something which can be communicated to matter, and which can be handed on from one piece of matter to another. Heat thus possesses the rank of a *quantity*, and we are led to seek *how much* heat a body gains or loses when its temperature changes. On the other hand, temperature is regarded rather as a quality which varies from one body to another, or from one part to another of the same body, when heat is being communicated to or abstracted from it, or which may vary, as we shall subsequently see, in consequence of actions taking place within the body itself, or performed on it from without.

It must, however, be distinctly remembered that what we directly *observe* is temperature and changes of temperature, and when the temperature of a body (free from other actions) rises we *say* it has received heat. The effect observed is the change of temperature, and the postulated cause is addition or subtraction of heat.

The use of the term force in dynamics is somewhat of the same nature; what we really observe is motion and changes of motion, or changes in the relative positions of bodies. To account for change of motion the idea of force is introduced, and a measure is adopted. Once a definite system of measurement is laid down the vagueness of the term disappears, and the meaning of the force on a body becomes perfectly clear and distinct. So to account for changes of temperature the idea of heat as something which can be added to or taken away from a body is introduced, and a measure of heat as a quantity must also be adopted. For this purpose a unit is essential, just as in the measurement of length or weight. This unit is more or less arbitrary, and for the purpose of definite measurement

may be chosen in connection with any one of the effects attributed to heat.

In popular language the word heat has a somewhat lax usage. It is sometimes used to denote a high temperature, as in the phrases, "white heat," "tropical heat," and "blood heat." Commonly, however, it is used either to express the sensations experienced in presence of hot bodies, or else the ultimate cause of those sensations, and in this latter sense it is used in such phrases as "the theory of heat" and "the science of heat." In the theory of heat we inquire into the nature of the process by which the various effects attributed to heat are brought about, and seek to determine the mechanism by which one body becomes warmer while another becomes colder, or, as we say, the process in operation when heat enters or leaves a body.

In saying that the heat of a body increases with its temperature, or that a body loses heat in cooling, we tacitly attribute to heat a positive character, so that its presence produces warmth and its absence cold. The word cold, then, has a negative character, and merely refers to the absence of heat. As the ideas of heat and cold are derived from the sensations, the positive value of either might be regarded as the negative value of the other, and the presence of one might be regarded as the absence of the other. As far, then, as the sensations alone direct us, either or both might possess a positive character. We have no more experience of the total absence of heat, or greatest possible coldness, than we have of the greatest possible accumulation of heat or greatest possible hotness. The general opinion has long been that the sensation of coldness is due to loss of heat and that of warmth to the gain of heat. In early times, however, this did not appear so evident. When the hand is placed on a piece of ice, instead of heat being given by the hand to the ice, some philosophers supposed that a cold body possessed minute "particles of frost" or "frigorific particles," which passed from cold bodies into those which are warmer, and these spiculæ or little darts were supposed to account for the acutely painful sensation, and some other effects, due to intense cold.

21. Unit of Quantity.—The unit of heat generally employed is the quantity of heat necessary to raise the temperature of one gramme of pure water one degree centigrade. The same quantity of heat will be given out by one gramme in cooling 1° C. This, however, is not *a priori* evident. It is not a truism, but a truth established by experiment.

In the case of a uniformly-heated mass of water it is legitimate to assert that the quantity of heat contained in any one gramme of it is

the same as that contained in any other, and that the quantity of heat required to raise any one cubic centimetre of it, from any one definite temperature to any other, will be the same, under the same conditions, as for any other cubic centimetre. Thus, if the quantity of heat necessary to raise the temperature of a gramme of water, or any other substance, through a given interval of temperature, be denoted by q, then the quantity required to raise m grammes through the same range of temperature will be mq.

We cannot, however, assert that the quantity of heat necessary to raise the temperature of a body 1° is the same at all parts of the scale, or that the quantity given out by a body in cooling from 50° to 40° is equal to that given out by the same body in cooling from 25° to 15°. We have no reason to expect *a priori* that the quantity of heat is proportional to the interval of temperature. In defining the unit of heat above we have only stated that it is the quantity of heat necessary to raise one gramme of water 1° C. We have not stated at what part of the scale the degree is to be taken, whether it is the interval from 0° to 1°, or from 4° to 5°, or any other. In strictness this ought to be done, but in practice it is found that there is scarcely any appreciable difference, whatever be the degree chosen. Experiment proves that very approximately the same quantity of heat is required to raise a given mass of water 1° in temperature at any part of the scale between the freezing point and the boiling point (see Art. 153). It is well, however, to be accurate, and to fix a particular degree, say from 4° to 5°. According to this system a quantity Q of heat means the quantity which will raise Q grammes of water from 4° to 5° C., and not the quantity which will raise one gramme of water Q° C. The latter happens, however, as we have already said, to be very approximately equal to the former.

Other units of heat might be, and actually have been, chosen depending on other effects of heat on matter, such, for example, as the change of state. These will be noticed later on.

It is important to remark that we can now speak definitely of the quantity of heat required to raise a body from one temperature to another, but that the "quantity of heat in a body" is still without meaning. So far the quantity of heat in a body is as indefinite as the quantity of sound in a bell, or the height of an object above an unknown plane.

22. Sensible Heat and Latent Heat.—As already noticed, when two bodies at different temperatures are placed in contact, heat is supposed to pass from the hotter to the colder, but either of two things may happen. Either the temperature of the colder may rise, while

that of the warmer falls, or a change of state may occur in one while the temperature of the other alone varies. In the former case, that is, when the heat which leaves one enters the other and increases its temperature, the heat which enters it exhibits itself in the corresponding rise of temperature, and is said to be *sensible* heat. That is, it can be detected by the thermometer. In the second case, however, the warmer body is continually losing heat, but the temperature of the colder remains fixed. Its state merely changes. The heat which it receives does not exhibit itself by any rise of temperature, and cannot be detected by the thermometer. It becomes, as Black said, latent, and is consequently termed *latent heat.* In illustration of this point it may be well to describe here the experiment by which Black[1] was led to his doctrine of latent heat.

Black's experiment.

Having exposed a mass (5 oz.) of ice-cold water in a vessel suspended in a large hall, he noticed that the temperature rose very nearly 4° C. (7° F.) in half an hour. He also exposed an equal mass of ice in the same room under the same conditions and found that it required ten hours to melt. Now the ice receives heat from the room, and the quantity received during ten hours was only sufficient to melt it. This quantity may be calculated from the experiment on the ice-cold water, which received as much heat in half an hour as raised its temperature almost 4° C. Assuming that the melting ice received heat at the same rate, the total quantity required to melt it will be nearly twenty times that required to raise an equal weight of water 4° C., or almost as much as would raise eighty times its weight of water one degree centigrade.[2] This shows roughly that about eighty units of heat are required to convert a gramme of ice into a gramme of ice-cold water, without changing the temperature. That is, eighty units of heat have disappeared or become latent in effecting the change of state from solid to liquid. For this reason eighty is said to be the latent heat of ice, meaning that eighty units of heat are necessary for the liquefaction of ice per gramme.

Black also determined the latent heat of ice by mixing warm water and ice in known quantities and noting the change of temperature. Allowing for the influence of the containing vessel he found by this method 79·4—a number remarkably near that given by the best recent determinations.

Before the time of Black it was universally considered that when

[1] Black, *Elements of Chemistry*, vol. i. p. 116. Published by John Robison, Edinburgh, 1803.

[2] Black used a Fahrenheit thermometer, a description of which will be found in Chap. II.

a solid changed into a liquid, or a liquid into a vapour, no continued supply of heat was necessary for the transformation, and that all the heat supplied exhibited itself in a corresponding rise of temperature. In other words, heat was always sensible, and could be detected by the thermometer. Black[1] says: "This was the universal opinion on this subject so far as I know when I began to read my lectures in the University of Glasgow, in the year 1757. . . . The opinion I formed from attentive observation of the facts and phenomena is as follows. When ice, for example, or any other solid substance, is changing into a fluid by heat, I am of opinion that it receives a much greater quantity of heat than what is perceptible in it immediately after by the thermometer. A great quantity of heat enters into it on this occasion without making it apparently warmer when tried by this instrument. This heat, however, must be thrown into it, in order to give it the form of a fluid; and I affirm that this great addition of heat is the principal and most immediate cause of the fluidity induced."

"And on the other hand, when we deprive such a body of its fluidity again, by a diminution of its heat, a very great quantity of heat comes out of it, while it is assuming the solid form, the loss of which heat is not to be perceived by the common manner of using the thermometer."

Sensible and latent heats are thus very analogous to kinetic and potential energies. When work is spent in increasing the velocity of, or generating motion in, any body, the work so spent becomes visible, or sensible, in the motion of the body, and it is analogous to sensible heat. When, on the other hand, work is spent in raising a weight from the surface of the earth, or in changing the distances between the parts of a mutually-attracting system, the work so spent is not visible as any motion of the system but has as it were become latent, or potential, as it is termed. That some real relation here exists, and not merely an analogy, will probably appear as a knowledge of the facts accumulates.

23. Specific Heat and Thermal Capacity.—Having laid down a system of measurement of quantities of heat, the question which immediately presents itself is whether equal quantities of heat raise the temperatures of equal masses of different substances by the same amount, or if any relation exists between the quantities of heat given to equal masses, or equal volumes, of different substances, and the corresponding changes of temperature. If equal weights of the same substance (water, for example) at different temperatures be mixed,

[1] Black, *loc. cit.*

the temperature of the mixture is the arithmetic mean of those possessed by the two components before mixture (or very approximately so). The quantity of heat given out by the warmer mass in falling through a certain range of temperature raises the colder mass through an equal range. The case is very different if two dissimilar substances are mixed together. The change of temperature of a body is not alone sufficient to determine the quantity of heat it has gained or lost. This quantity depends not only on the change of temperature but also on the nature of the substance, and for this reason different substances are said to have different *thermal capacities* or *specific heats*. This is strikingly illustrated in the case of mercury and water. Thus, if a pound of mercury at 80° C. be mixed with a pound of water at 20° C., the temperature of the mixture will be only about 22° C. This shows that the heat lost by the mercury in cooling through 58° will raise an equal weight of water through only 2°. In other words, the quantity of heat which will raise the temperature of a given weight of water 1° will raise the temperature of an equal weight of mercury nearly 30°, or the thermal capacity of water is about thirty times that of mercury.

The thermal capacity of a body is defined as the quantity of heat necessary to raise the temperature of the body 1° C., and the thermal capacity of a substance is the quantity of heat required to raise unit weight (one gramme) of the substance 1° C.

The specific heat of a substance is its thermal capacity compared with that of water; in other words, it is the ratio of the quantity of heat required to raise the temperature of a given weight of the substance 1°, to the quantity of heat which will raise the temperature of an equal weight of water 1°. When the unit of heat is that required to raise the temperature of unit weight of water 1°, the thermal capacity and the specific heat of a substance are expressed by the same number.

Before the time of Black it was commonly supposed that the quantities of heat required to change the temperatures of different bodies by the same amount were directly proportional to the quantities of matter in them, or that all substances had the same thermal capacity.

Black's opinion.

"But very soon (1760) after I began to think on this subject," says Black,[1] "I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive, to reduce them to equilibrium with one another, or to raise their temperatures by an equal number of degrees, are not in proportion

[1] Black, *Lectures on the Elements of Chemistry*, p. 79.

to the quantity of matter in each, but in proportions widely different from this. . . . This opinion was first suggested to me by an experiment described by Dr. Boerhaave (*Elements of Chemistry*). After relating the experiment which Fahrenheit made at his desire, by mixing hot and cold water, he also tells us that Fahrenheit agitated together quicksilver and water unequally heated. From the Doctor's account it is quite plain that quicksilver, though it has more than thirteen times the density of water, produced less effect in heating or cooling water to which it was applied than an equal measure of water would have produced. He says expressly that the quicksilver never produced more effect in heating or cooling an equal measure of water than would have been produced by water equally hot or cold with the quicksilver and only two-thirds of its bulk."

Black concluded, therefore, that quicksilver has a much less capacity for heat than water, and that different substances have different thermal capacities. The inference made by Dr. Boerhaave from the same experiment is very surprising. Seeing that the heat obviously was not distributed among different bodies at the same temperature in proportion to their masses, he concluded that it was distributed in proportion to their volumes, or that equal volumes of all substances have the same thermal capacity. This conclusion, as Black remarks, was contradicted by the very experiment on which it was founded, yet in it Boerhaave was followed and supported by Muschenbroeck.

The small capacity for heat of a dense body like mercury was considered by Black as a strong objection against the dynamical theory of heat, for if heat be motion, then in his opinion a dense body should contain much more of it than a rare one at the same temperature.

24. Thermometry by Quantities of Heat.—A perfectly scientific though inconvenient system of thermometry might be founded on the measurement of quantities of heat rather than on changes of volume. Thus, if we lay down any two definite temperatures, such as the melting point of ice and the boiling point of water under a definite pressure, or the melting point of any other solid, these temperatures will correspond to certain fixed marks on the stem of an instrument, such as the mercurial thermometer already described. If now the unit of heat be taken as the quantity of heat necessary to raise one gramme of water from one of these temperatures to the other, then n units of heat will raise n grammes of water through the same interval of temperature. It will be convenient to take the lower fixed temperature as that of melting ice, as ice-cold water is easily

procurable, and the other fixed temperature may be taken as corresponding to any fixed mark on the stem of the mercurial thermometer, say the division marked 1°.

If now we wish to compare the temperatures of two pieces of the *same* substance in the same physical state, it will be only necessary to find how many grammes of water[1] a gramme of each (or equal weights of each) will raise from 0° to 1° (our chosen fixed temperatures)—that is, the number of units of heat each will give out per unit mass in falling from their original temperatures to the upper fixed temperature. Equal differences of temperature will thus correspond to equal increments of heat, or the temperatures of two pieces of the same substance will be in the ratio of the quantities of heat required to raise unit mass of each from the upper fixed point to its present condition. For temperatures below the lower fixed point it will be necessary to find the weight of water which, in cooling from the upper to the lower fixed point, will raise unit mass of the substance from its present temperature to that of the lower fixed point. This point consequently becomes the zero of our new scale, and temperatures expressed by this system will be so much above the upper or so much below the lower fixed point.

So far we have only compared the temperatures by this system of different pieces of the *same* substance. This restriction was necessary because it is found that equal masses of different substances heated uniformly in the same enclosure or bath will give out very different quantities of heat in falling from their common initial temperature to that of the upper fixed point. This is expressed by saying that different substances have different thermal capacities per unit mass, or different *specific heats.* If, therefore, it is desired to make this system of thermometry generally applicable, a small carrier body, say a small metallic disc supported by a silk thread, may be employed, just as a proof plane is employed in the measurement of electrical potentials. If this small carrier be brought into contact with any body it will rapidly assume the temperature of the body; errors arising from the finite mass of the carrier and initial temperature difference between it and the body being neglected. The carrier may now be removed to the vessel containing the ice-cold water and the weight of water which it raises from zero to the upper fixed point estimated. By this means we can compare, or as it were weigh, the temperatures of different bodies.

In order that this system of thermometry should agree with that which measures equal increments of temperature by equal increments

[1] Perhaps it would be better to work with the quantity of ice melted.

of volume, it is necessary that equal expansions of the thermometric substance should correspond to equal increments of heat, or that the dilatation should be proportional to the quantity of heat received. Air and the permanent gases seem to be the only substances which satisfy this condition very closely, but between 0° and 100° C., and for some distance beyond these points, mercury, expanding in an ordinary soft glass envelope, also possesses this property. In general the dilatation of a body increases for equal additions of heat as the temperature becomes more elevated. Dulong and Petit[1] executed a series of experiments on this point. They measured the quantities of heat absorbed by various substances, and also the consequent dilatation, and they found that the expansion was not simply proportional to the quantity of heat, but that between the dilatation and the quantity of heat absorbed some complicated relation exists which depends on the nature of the substance. In the case of the permanent gases, however, Regnault[2] found that the change of volume under constant pressure was simply proportional to the quantity of heat received, and hence the system of thermometry here considered will agree with that registered by an air thermometer.

Expansion of gases.

For this and many other reasons the air (or rather perfect gas) thermometer is the only strictly scientific measurer of temperature, and all other thermometers ought to be standardised by direct comparison with it.

25. Thermometry by the Sense of Heat.—The sense of heat is a somewhat delicate test of the equality of temperature in the case of similar bodies, that is, of portions of the same sort of matter. Thus by the hand alone a very small difference in the temperatures of two water baths may be detected, especially by persons who have cultivated the sense of heat for this purpose. It is very different, however, when we touch in succession objects which are of dissimilar natures. Let us take the case of a room without a fire on a cold frosty day. All the objects in such a room will be at the same temperature. This may be tested by means of a thermometer. A metal paper weight will, however, when touched feel much colder than the paper on which it rests, and the wooden table will feel colder than the woollen tablecloth. In explanation of this, we regard the sensation of coldness as due to the loss of heat by the hand, and this is not simply dependent on the temperature of the body touched, but depends rather on the rate of loss of heat. The hand loses heat much more rapidly to the

[1] *Ann. de Chimie et de Phys.*, 2e, tom. ii. p. 240, 1816.

[2] *Relation des Expériences*, tom. i. p. 163 ; *Mémoires de l'Académie des Sciences*, tom. xxi.

metal paper weight than to the paper, and more rapidly to the wooden floor than to the carpet. The rate at which one body communicates heat to another at a lower temperature depends, as we shall see later on, not only on the difference of temperature, but also on the nature of the materials of which they are composed, and on their surfaces. The properties engaged are specific heat, and internal and external conductivities for heat.

It is rather surprising at first to find on touching some bodies, which we know to be at or below the freezing point, that they actually feel warm; a moment's reflection, however, leads to an explanation. Our bodies part with heat to all other bodies at a lower temperature, and on a cold day we are constantly giving out heat to the air. If, then, we touch any body which draws off heat more rapidly than the air it appears cold when touched, but if it draws away the heat less rapidly than the air from the hand it will feel warm by comparison. It is for a similar reason that we feel much warmer when clothed than when naked, and that woollen stuffs are employed for bedcovers.

The estimation of temperature by the sense of heat depends upon so many variable conditions, the state of the observer included, that it cannot be used with any certainty. In illustration of this a well-known experiment is often cited. Thus if one hand be placed in a basin of hot water, while the other is placed in a basin of cold water, and then the two are simultaneously placed in a basin of tepid water, this latter will appear cold to the hand which was in the hot water and hot to that which was placed in the cold. This arises from the fact that the tepid water is colder than the surface of the hand which was in the hot water, and warmer than that which was placed in the cold water. The result is that one hand gives up heat to the tepid water, while the other receives heat; the former accordingly becomes chilled, while the latter is heated. When cultivated, however, not only can very small differences of temperature be detected in similar substances by the sense of heat, but a memory of certain definite temperatures can be permanently acquired. This happens in the case of bath attendants and hospital attendants, and those engaged with hot liquids in various manufactories, such as dyeworks. Such persons can tell to within less than a degree centigrade whether a bath or a poultice is at "blood heat," or "fever heat," or some other definite temperature to which they are accustomed.[1]

26. Remarks on the Definition of Temperature.—In concluding this section it may be well to call attention to the great importance of a clear definition and a thorough understanding of the exact meaning

[1] Sir William Thomson, *Math. and Phys. Papers,* vol. iii. p. 130.

of each term used in any branch of science. Without this progress is hopeless, and all reasoning on the subject becomes a meaningless tangle of words, more calculated to confuse than enlighten.

Attention has already been directed to the method of explaining the seen by means of the unseen, and the known by means of the unknown. A similar and perhaps more pernicious habit which still lingers is the definition of scientific terms by means of other words to which no distinct meaning can be assigned. As an example take the following definition: "The temperature of a body is the energy with which the heat in a body acts in the way of transferring or communicating a portion of itself to other bodies." In this definition two new words, energy and heat, are introduced, and the idea of "the energy with which the heat in a body acts," as well as the conception of the transference of heat from one body to another. Until the new words, as well as the ideas involved, are thoroughly explained, such a definition can give no distinct idea of what the word temperature means. The student would be better without any definition than such a one. A mystifying string of words can only addle and discourage him at the outset of a new and difficult subject.

Other and no less objectionable forms of definition ordinarily met with are "the power of a body to communicate heat to other bodies," or, "the greater or less extent to which it tends to impart sensible heat to other bodies." The first essays to explain the word temperature by the introduction of the word power. Now the word power with reference to engines has a perfectly definite meaning, but in ordinary language it seems to enjoy an almost universal application. It is so thoroughly indefinite that it does not attract the attention of the student, especially when mixed up with scientific words, and he passes on without seeing that such a sentence really has no meaning. If we take "the power of a body" referred to above as meaning the quantity of heat it will give to other bodies, we see at once that this will depend not only on the hotness of the body, but on its mass and the thermal capacity of its material as well as on the "other bodies." If we take the power as the rate of giving out heat, we are again in similar difficulties, for the rate of loss of heat will depend upon the nature of the surface as well as that of the material, and by no means on the hotness alone of the body. Similar remarks apply to the second definition. It perhaps excels the first in indistinctness. The "greater or less tendency of a body" seems to contain an idea, but it is not easy to understand its precise meaning!

The last form of definition which we shall consider is much

thermal state of a body considered with reference to its power of communicating heat to other bodies." The "power of communicating heat," as has been already pointed out, either means nothing or is entirely incorrect. The thermal state of a body, if it means anything, means the hotness of a body, and the definition implies that the temperature is the hotness considered in a certain aspect.

Another strange inversion of ideas is also generally met with. It occurs in the consideration of difference of temperatures. Thus it is stated that two bodies are said to be at different temperatures when, if placed in contact, heat passes from one to the other. Now it is in the reverse order that the ideas are actually obtained. What we directly *observe* is temperature and change of temperature (see Art. 20). When the temperature of a body changes we account for it by supposing that heat has left or entered it. We do not *observe* the heat passing from one body to another, and find that as a consequence the temperature changes. In order to find out which of two bodies is at the higher temperature we do not place them in thermal communication, and observe if "heat" flows from one to the other. The flow of heat is an assumed phenomenon arising from the observed change of temperature, and is asserted merely because we say that when the temperature of a body is changing it is gaining or losing heat, or that increase of temperature is accompanied by, or caused by, a gain of heat, and fall of temperature by a loss.

A theory may be wrong, but it certainly ought to be clear and distinct, and should be expressed in language which can be easily understood. The definitions sometimes met with often escape the merit of being false by being expressed in words which have no assignable meaning. In the theory of heat ambiguity in this respect probably arises from the fact that during the present century a new theory has been built up while the old doctrine lingered on. Terms which were distinct in the latter have been retained with a very different signification in the former, and an imperfect apprehension of their exact meaning somewhat liberally perplexes the student.

SECTION III

EARLY THEORIES OF HEAT

27. Two Theories prevalent.—From the dawn of science to the present century two rival hypotheses regarding the nature of heat were generally entertained, neither of them, however, being founded on any sufficiently established basis. According to one, known as the caloric theory, heat was supposed to be a subtle elastic fluid which permeated the pores of bodies, and filled the interstices between the molecules of matter. The other doctrine, which is as old as the ancient Greeks, and contains the germ of the modern theory, supposed heat to be due to a rapid vibration of the molecules of a body, and consequently attributed heat to motion. The supporters of this theory seem to have been long in a miserable minority.

28. Lord Bacon.—The first philosophic attempt at the formation of a theory founded on observation seems to have been made by Lord Bacon[1] in a treatise which he offered as a model of the proper manner of prosecuting investigations in Natural Philosophy. In this treatise he sums up all the principal facts then known relating to heat, or to the production of heat, and after a cautious and mature consideration of these he endeavours to form a well-founded opinion of their cause. On deliberating over the various ways in which heat is produced by friction and percussion, the only conclusion he could draw from the whole facts was the very general one that "heat is motion."

The opinion of Lord Bacon was adopted very generally, but with two different modifications. The greater number of his followers in England supposed that the motion or tremor which constituted heat was in the small particles of the body, while the majority of continental philosophers supposed that the vibration was not that of the particles of the body itself, but rather of the particles of a subtle and highly elastic fluid, penetrating the pores of bodies, and interposed between their particles. This fluid they imagined to be diffused through the

[1] *De forma Calidi.*

whole universe, pervading with ease the densest bodies, and in the opinion of some, when modified in certain ways, produced the phenomena of light and electricity.[1]

29. The Caloric Theory.—The other school of philosophers, however, was in power till the beginning of the nineteenth century. They held that heat was not due to motion, but to the action of a highly elastic and self-repellent fluid, which was all-pervading and universal. At first the only properties postulated were that it was highly elastic, and that its particles repelled each other very strongly. It was by this latter property of caloric, as the heat fluid was called later on, that bodies in combustion threw off heat and light. Subsequently Dr. Cleghorn introduced another property which was strongly favoured by Black, namely, that the particles of the caloric, though self-repellent, were yet strongly attracted by the particles of ordinary matter, and that different kinds of matter attracted the caloric with different degrees of force. Thus, among any system of bodies, an equilibrium would be established between the self-repulsion of the caloric and the attractive influence exerted on it by the matter, and caloric would pass from one body to another until this equilibrium was established.

The fundamental quality demanded for the heat fluid was that it was indestructible and uncreatable by any process. Bodies became warmer when caloric was added to them, and grew colder as it left them. In this respect it possessed the essential property of ordinary matter—a property also attributed to energy, which replaces it in the dynamical theory.

As to the possession of the other property of matter—namely, weight—a great diversity of opinion existed. Some philosophers held that caloric had weight, while others held that it had not. Experiments on this point were difficult and doubtful, and contradictory results were often obtained. At the close of the eighteenth century, however, the general opinion in the best informed circles was that the heat fluid was imponderable, and in this respect it differed from ordinary matter. Count Rumford[2] finally settled the point by a set of delicate and most instructive experiments, from which he concluded that "all attempts to discover any effect of heat upon the apparent weights of bodies will be fruitless."

That equal weights of different substances require different amounts of caloric to raise their temperature through the same interval was

[1] See Black's *Lectures on the Elements of Chemistry*, vol. i. p. 33.

[2] Rumford, "An Inquiry concerning the Weight of Heat," *Phil. Trans.*, 1799; and *Complete Works*, vol. ii. p. 2.

easily explained by the calorists on Cleghorn's supposition, that different kinds of matter attract the caloric differently, and consequently it was reasonable to suppose that some substances would absorb greater quantities of caloric than others in rising through the same range of temperature. Other very plausible explanations of physical phenomena were arrived at by the partisans of this theory. Thus the general expansion of bodies by heat followed as a natural consequence, for, the caloric being a self-repellent fluid, when the quantity in any body increased it was to be expected that the self-repulsion of this fluid would cause an increase of volume. Even when heating caused contraction, it was not difficult to find analogies in support of the theory. Thus contraction occurs when water and alcohol are mixed, and in alloys of copper and tin, and in some chemical combinations the volume of the combination may be less than that of either constituent.

To explain his doctrine of latent heat, Black supposed that caloric could not only exist in the free state, that is as sensible heat, but also in combination with matter, in which case it became latent and inactive. It could not then be detected by the thermometer. From this point of view water is the result of a combination of the substance of ice with a certain proportion of caloric, and steam is a combination of water with a further quantity of caloric. This doctrine, proposed by Black, was not however generally accepted. There were many who thought that liquefaction was not attributable to heat alone. They considered, for example, that water was a fluid from an essential quality, depending upon the supposed spherical shape of its particles, and that the freezing of it depended upon the introduction of some extraneous substance, such as frigorific particles, etc., and this view was supported in the case of water by the increase of bulk in freezing.[1]

The conduction of heat—that is, its transference from one body to another in contact with it, or from one part to another of the same body—also presented no difficulty, for the caloric was supposed to flow from places of higher to places of lower temperature, as a liquid flows from places of higher to places of lower level. The flow of the caloric from higher to lower temperatures was a consequence of the supposed mutual repulsion of its particles.

So far the explanations of the calorists were certainly satisfactory, although in some cases they were cumbrous and difficult of application. We shall, however, see immediately, as facts accumulate, that cases will come to hand which cannot be explained by the caloric doctrine, at least without radical changes in its fundamental postulates.

[1] This view was defended by Prof. Muschenbroeck, *Phys. de Aqua.*

SECTION IV

THE DYNAMICAL GENERATION OF HEAT

30. Heat developed by Friction.—That heat may be freely developed by friction seems to have been well known to all classes of men from the earliest times. Every schoolboy is well acquainted with the fact that a brass nail may be heated to a painful degree by rubbing it on a wooden seat. Friction, indeed, is the ordinary resource of the savage in lighting his fire.[1]

It is on account of the great heat developed by friction that such precautions are taken to keep the wheels of railway carriages well greased, and even with the utmost provision against it the wheels and axles of express trains become so warm that a stoppage or slackening of speed becomes necessary. Outbreaks of fire arising from the heat developed by friction between the wheel and axle of a rapidly-driven carriage have not infrequently occurred. An analogous development of heat is produced by percussion. A soft iron rod rapidly hammered on an anvil may be heated by an experienced hand to the point of incandescence, while a few strokes will warm it sufficiently to light a match. In like manner a bullet is found to be considerably heated after striking a target. The flash of light often seen when an iron shot strikes a target shows that the heat developed by the impact is sufficient to raise to incandescence the scattered dust and particles abraded by the collision.

In like manner there is a development of heat by friction in

[1] The Gaucho of the Pampas presses the blunt end of a flexible rod about 18 inches long against his breast, and the other end, which is pointed, he places in a hole drilled in a piece of dry wood. Bending the rod by the pressure of his body, he seizes the curved part and turns it rapidly round, till the heat developed by the friction of the rod against the block of wood is sufficient to produce ignition. In Australia and Tasmania ignition is produced by the rapid twirling of the pointed stick between the palms of the hands, and among the Esquimaux one person presses the end of the rod against the piece of wood, while another produces a rapid rotation to and fro by means of a thong.

liquids. In the ordinary process of churning there is a considerable rise in the temperature of the milk before the operation is completed. Water, or any other liquid, may be heated in the same manner, and it was by an. experiment of this kind that Joule first determined the dynamical equivalent of heat, that is, the relation between the quantity of work spent in churning and the quantity of heat developed by the process.

31. The Fire Syringe.—One of the most interesting illustrations of the dynamical generation of heat is furnished by the fire syringe. This instrument consists of a stout cylindrical glass tube, accurately bored and quite smooth within. An air-tight piston is fitted into it, so that by forcing the piston forward the air in the tube is compressed. When the air is thus forcibly compressed, heat is suddenly generated, and the rise of temperature thus developed may be sufficient to ignite a piece of tinder attached to the inner end of the piston.

If a pellet of cotton wool, moistened with bisulphide of carbon, be thrown into the tube and then immediately ejected, so that a mixture of its vapour and air fills the tube, a flash of light will be seen on suddenly compressing the contents. The heat developed by the compression has been sufficient to ignite the vapour.

The converse operation—the development of cold or destruction of heat—may be also illustrated by means of this or some similar apparatus.[1] Thus if the gas be compressed, and after attaining a fixed temperature be allowed to expand, pushing the piston before it, so that work is done against the external pressure, a noticeable fall in the temperature of the gas will occur.

That the temperature of a gas is elevated by sudden compression and reduced by expansion seems to have been first noticed by Dr. Cullen and Dr. Darwin.[2] This fact being once noticed would naturally lead to an inquiry as to the quantity of heat developed by a given compression, or the relation between the amount of compression and the change of temperature or quantity of heat developed. Dalton[3] was the first to estimate this change of temperature with some degree of accuracy, and from his experiment he concluded that when air is compressed to one half its bulk a heating

[1] For example, by allowing air to escape from a vessel in which it has been compressed. The cooling effect when small may be registered by some sensitive thermoelectric apparatus. The cooling produced by the expansion of carbonic acid gas when escaping under high pressure into the atmosphere, is so great that the escaping gas becomes not merely liquefied but actually solidified.

[2] Joule, *Phil. Mag.*, May 1845.

[3] Dalton, *Memoirs of Lit. and Phil. Soc. of Manchester*, vol. v. pt. 2, pp. 251-525.

of 50° F. occurs, with a similar cooling when a corresponding rarefaction takes place.

Subsequently Dulong[1] showed that equal volumes of all gases taken at the same temperature and pressure evolved (or absorbed) the same quantity of heat when suddenly compressed (or dilated) by the same amount.

32. Explanation of the Calorists.—That heat is developed by friction and percussion was well known to the supporters of the caloric theory, and accounted for by well-framed hypotheses. Thus any body in its normal state possessed a certain capacity for heat, and contained a certain quantity of caloric at a definite temperature. Percussion altered the condition of the substance and lessened its capacity for heat. Some of the caloric was squeezed out of it, and, being thus set free, manifested its presence by the rise of temperature. Similarly, in the hammering of a nail, the caloric was simply hammered out of the pores of the iron. The molecules of the matter were driven closer together, and the caloric was ejected. In the case of friction, however, part of the material was abraded or rubbed into powder, and the calorists postulated that the capacity for heat of the powder was smaller than that of the solid from which it was abraded; there was thus an evolution of heat.

This reasoning is strictly philosophical if the assumptions on which it is based be true, viz. that the capacity for heat is less in the state of powder than in the solid state; and further, that heat is indestructible, or that the quantity of heat fluid in the universe remains permanently the same. The calorists did not, however, appeal to experiment to prove that the capacity of a body for heat was less in the dusty state than in the block. If they had done so, they would have found their postulate overthrown, and would have been forced to abandon their theory, or devise some other explanation of the heat developed by friction. The production of heat by the friction of liquids, as in the process of churning, could scarcely be explained on the same lines. Here there is no abrasion, no apparent change of state or powdering of the material, and consequently no room for the postulate that its heat capacity is diminished by the process which generates the heat.

The peculiarity of the heat supply obtainable by friction is that it appears to be inexhaustible, so that the quantity of heat obtainable by rubbing together two bodies which do not abrade would be infinite. This cannot possibly be explained by the supposition that the heat capacity of the substance is less in the powdered or com-

[1] Dulong, *Ann. de Chimie*, 2e, tom. xli. p. 156, 1828.

pressed than in the original state, but its explanation must be looked for in the action or agent which causes the rubbing. From this point of view the heat developed is the result of the work done by the agent producing the rubbing.

33. Rumford's Experiment.—The first experimental investigation into the true nature of heat was made by Count Rumford[1] in 1798.

While engaged in the boring of brass cannon at the military arsenal in Munich, he was struck by the high temperature of the metallic chips thrown off, and by the excessive development of heat during the process. In order to investigate the matter thoroughly he prepared a hollow gun-metal cylinder, formed in the waste head[2] of a cannon, and mounted it so that it could be rotated by horse-power on a horizontal axis, while a blunt steel borer pressed against its bottom. The cylinder was covered with a thick coating of flannel to prevent loss of heat, and a small radial hole to contain a thermometer was drilled into the bottom, and terminated at its centre. The bulb of the thermometer was thus at the middle point of the thick bottom of the cylinder,[3] and the stem projected from its side.

At the beginning of the experiment the thermometer stood at 60° F., and after half an hour, when the cylinder had made 960 revolutions, the temperature was found to be 130° F., which fairly represented the mean temperature of the cylinder.

He now removed the metallic dust or scaly matter abraded by the friction from the bottom of the cylinder, and found it weighed only 837 grains troy. "Is it possible," he exclaims, "that the very considerable quantity of heat produced in this experiment—(a quantity which actually raised the temperature of above 113 lbs. of gun-metal

[1] Rumford, *Phil. Trans.*, 1798. Count Rumford's name was Benjamin Thomson. He was born in 1753 at Woburn, near Boston, and was driven to Europe for his loyalty during the rebellion of the British colonies in America. He effected various important reforms in Bavaria, and chose the title by which he is generally known (and which was conferred on him for his services) from a village in New Hampshire, now called Concord, where he was obliged to leave his wife and infant daughter.

[2] The *verlorner kopf*, or waste head, was a solid mass about 2 feet long, projecting beyond the muzzle of the gun. This was cut off before boring. It was cast with the gun in order that its weight on the lower parts might make them compact. Without this precaution the metal in the neighbourhood of the muzzle would be more or less porous.

[3] The external diameter of the cylinder was $7\frac{3}{4}$ in., and its length 9·8 in. The diameter of the internal cavity (which was drilled out) was 3·7 in., and its depth 7·2 in., so that the bottom was 2·6 in. thick. The borer was a flat piece of hardened steel 4 in. long, 0·63 in. thick, and nearly as wide as the cavity, viz. 3·5 in. It was kept fixed and pressed against the bottom of the cylinder by means of a strong screw with a pressure of 10,000 lbs.

at least 70 degrees of the Fahrenheit thermometer, and which, of course, would have been capable of melting $6\frac{1}{2}$ lbs. of ice, or of causing near 5 lbs. of ice-cold water to boil)—could have been furnished by so inconsiderable a quantity of metallic dust, and this merely in consequence of *a change* in its capacity for heat? . . . But without insisting on the improbability of this supposition, we have only to recollect that from the results of actual and decisive experiments, made for the express purpose of ascertaining that fact, the capacity for heat of the metal of which great guns are cast is *not sensibly changed* by being reduced to the form of metallic chips in the operation of boring cannon, and there does not seem to be any reason to think that it can be much changed, if it be changed at all, in being reduced to much smaller pieces by a borer that is less sharp."

This test was not, however, conclusive to the calorists. It was not sufficient to prove, as Rumford did prove, that the capacity for heat of the solid metal was the same as that of the chips. It was still necessary to prove that equal masses of the solid metal and the abraded dust always contain the *same quantity* of heat when at the same temperature. A calorist might say that although metal and the dust possess the same thermal capacity at the same temperature, yet the solid metal contains a greater quantity of heat than the dust, the difference having been evolved during abrasion. It has been stated that this point might have been settled by melting equal weights of the two, and observing the quantity of heat necessary to change equal weights of the solid and abraded dust into fused metal. If these are equal, and if it be allowed that the fused mass is exactly the same in all respects in one case as in the other, then the dust and the solid metal will contain equal quantities of heat per unit weight when at the same temperature. A similar test would be by solution in an acid, and observation of the heat of combination. Rumford, however, did not stake his opinion on such experiments as these. He adhered firmly to the one main point and feature of the experiment, namely, that the supply of heat is inexhaustible. If the heat were rubbed out of the material, a stage would be reached at which all its heat would be exhausted. No such stage was ever observed. The supply was as free and copious at the end of the experiment as at the beginning. All that was necessary was the continued working of the machinery. The quantity of heat obtained depended in no way on the amount of rubbing or hammering the brass had previously received; it depended only on the work spent in friction during the experiment (see further, p. 43).

Rumford also proceeded to determine if the exclusion of the air

from the cylinder had any effect. For this purpose he closed the end of the cylinder with a tight-fitting collar so that the air had no access to the interior during the experiment, but he found no observable difference in the result. He also placed the cylinder in a wooden box filled with water in such a manner that it could revolve either water-tight or open, while the borer pressed against its bottom as before. At the beginning of the experiment the temperature of the water was 60° F. One hour after the machinery had been set in motion the temperature of the water, which weighed 18·77 lbs. ($2\frac{1}{4}$ gallons), was 107° F., or had been raised 47° F. In thirty minutes more the temperature was 142° F., and at the end of two hours from the beginning of the experiment the temperature was 178° F., while in $2\frac{1}{2}$ hours the water actually boiled!

He then proceeded to calculate the quantity of heat possessed by each part of the apparatus at the conclusion of the experiment, and found that the total was sufficient to raise 26·58 lbs. of ice-cold water to the boiling point. This, together with the duration of the experiment, gave the rate at which the heat was generated to be "greater than that produced in the combustion of nine wax candles, each three quarters of an inch in diameter, all burning together with clear bright flames."

"One horse," he adds, "would have been equal to the work performed, though two were actually employed. Heat may thus be produced merely by the strength of a horse, and in a case of necessity this might be used in cooking victuals. But no circumstance could be imagined in which this method of procuring heat would be advantageous; for more heat might be obtained by using the fodder necessary for the support of the horse as fuel."

"In meditating over the results of all these experiments, we are naturally brought to the great question which has so often been the subject of speculation among philosophers, namely—

"What is Heat?—is there any such thing as an *igneous fluid*? Is there anything that can with propriety be called *caloric*?"

"We have seen that a very considerable quantity of heat may be excited by the friction of two metallic surfaces, and given off in a constant stream or flux *in all directions*, without interruption or intermission, and without any signs of diminution or exhaustion. . . ."

"In reasoning on this subject we must not forget that most remarkable circumstance, that the source of the heat generated by friction in these experiments appeared evidently to be *inexhaustible*."

"It is hardly necessary to add that anything which any *insulated* body or system of bodies can continue to furnish without *limitation*

cannot possibly be a *material substance*; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments except it be MOTION."

34. Davy's Experiment.—The fatal blow to the caloric theory was delivered by Humphry Davy, who first showed that two pieces of ice may be melted by simply rubbing them together. Davy reasoned that if ice can be liquefied by friction, a substance (water) will be produced, which is allowed by all parties to contain a far greater amount of heat than the ice. Liquefaction will then conclusively demonstrate the generation of new heat. He tried the experiment and succeeded. He says:[1] "I procured two parallelopipedons of ice (the result of the experiment is the same if wax, tallow, resin, or any substance fusible at a low temperature be used) of the temperature 29° F., 6 inches long, 2 wide, and $\frac{2}{3}$ of an inch thick; they were fastened by wires to two bars of iron. By a peculiar mechanism their surfaces were placed in contact, and kept in a continued and violent friction for some minutes. They were almost entirely converted into water, which water was collected and its temperature ascertained to be 35° F., after remaining in an atmosphere of a lower temperature for some minutes. The fusion took place only at the plane of contact of the two pieces of ice, and no bodies were in friction but ice. From this experiment it is evident that ice by friction is converted into water, and according to the supposition of the calorists its capacity is diminished; but it is a well-known fact that the capacity of water for heat is much greater than that of ice, and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction consequently does not diminish the capacities of bodies for heat."

Davy then proceeded to determine if the heat which produced the liquefaction could have been derived from the air or bodies in contact with the ice. For this purpose he caused the experiment to be performed by clock-work under the exhausted receiver of an air-pump surrounded with ice; but in this case also liquefaction was produced as before. He consequently concluded that heat is *produced* by friction, and that caloric, or the matter of heat, does not exist; that "a motion or vibration of the corpuscles of bodies must be

[1] Davy, "Essay on Heat and Light and Combinations of Light," *Complete Works*, vol. ii. p. 11. This was his first contribution to science, and was published in 1799 in the *Contributions to Physical and Medical Knowledge*, principally from the west of England. Collected by Thomas Beddoes, M.D.

necessarily generated by friction and percussion. Therefore we may reasonably conclude that this motion or vibration is heat. . . . Heat then . . . may be defined as a peculiar motion, probably a vibration of the corpuscles of bodies tending to separate them."

The minds of scientists were, however, so imbued with the caloric doctrine that the experiments and arguments of Davy attracted but little attention. They were even treated by some as wild and extravagant speculations. Even Davy himself did not seem to be confident. His subsequent writings do not bear the mark of complete conviction which characterises so unmistakably those of Rumford, and it was not until 1812 that he distinctly laid down[1] that

"The immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

Position of the calorists.

Both Rumford and Davy might, however, have been successfully met by any calorist who was willing to abandon some of the less essential parts of the doctrine. When heat is generated by friction or compression, the calorists accounted for it by asserting that the capacity of the material for heat is diminished, or that the heat is rubbed or squeezed out of it. Now let us suppose that it is proved beyond doubt that this is not the case. How then is a calorist to explain the evolution of heat in Rumford's experiment? By the fundamental tenets of his doctrine he is bound to consider heat as indestructible and uncreatable; but in this experiment a constant stream of heat flows from the parts in friction as long as the motion continues, and no equivalent loss of heat can be detected elsewhere. Any competent reasoner will therefore turn to the agent which keeps the machinery in motion. The calorist will be forced to state that the heat evolved in Rumford's experiment comes from the horse, and in making this assertion his position will be as strong, but scarcely so acceptable or rational, as that of his opponent. Briefly stated, the position of the calorist would be that heat is an imponderable fluid which cannot be created or destroyed, and therefore if heat appears to be generated in any mechanical process it must be derived from the agents or sources which maintain that process. The opponents of the caloric theory, on the other hand, assert that heat is not a fluid, but may be developed by the expenditure of work or energy. While one party might say that the caloric (or heat) is derived from the horse in Rumford's experiment, the other party maintains that energy is derived from the horse, and the heat which is evolved is the equivalent of it. The fundamental postulate of modern science con-

[1] Davy, *Elements of Chemical Philosophy*, p. 94.

cerning energy is that it cannot be created or destroyed, and this is exactly the property demanded for caloric. The horse in Rumford's experiment supplies something to the machinery which possesses exactly the same fundamental quality of permanence according to both schools.

35. The Dynamical Equivalent of Heat — Joule's Experiments.—That some relation existed between the work spent in driving the apparatus, and the heat developed, in Count Rumford's experiment had doubtless floated before the minds of many philosophers before either the correct enunciation or the exact experimental determination of this relation was made. A rough estimation indeed of this relation may be obtained from the experiment actually performed by Rumford.[1] The accurate investigation of the whole subject was taken up by Dr. Joule of Manchester in the year 1840, and continued for a long period with the highest experimental skill in several distinct investigations. The object of Joule's inquiry was to determine exactly the quantity of heat developed by the expenditure of a known amount of work, when this work is spent solely in producing heat by friction.

The method employed was practically a modification of that used by Rumford in showing that heat is developed when work is spent in friction. The modification consisted in the adoption of accurate methods for estimating the work spent and the heat generated. The heat was produced by friction of a brass paddle revolving in water contained in a specially constructed brass vessel, so that the water was heated by a kind of revolving-churn process, and the temperature was registered by means of a delicate mercurial thermometer. The paddle was driven by two leaden weights attached to a doubled cord passing over two pulleys, and the work spent in turning it was estimated from a knowledge of the mass of the weights and the height through which they descended.

After all corrections[2] were made, Joule decided that his mean result was 772 foot-pounds per degree Fahrenheit between the temperatures 55° and 60° F. That is, the work done in raising a weight of one pound through 772 feet in the latitude of Manchester will, if spent in friction (between brass and water), raise

[1] Thus Rumford estimated the thermal capacity of the water and apparatus as equivalent to that of 26·58 lbs. of water. Further, one horse was sufficient to turn the machinery and change the temperature of this mass from 33° to 212° F. in two and a half hours, the rate of increase of temperature being about 1°·3 per minute. This gives 847 foot-pounds as the dynamical equivalent, a number which is only about 10 per cent in excess of Joule's estimate.

[2] Except reduction to the air thermometer, see Chap. VIII., Section I.

the temperature of one pound of water one degree Fahrenheit. The unit of heat being the quantity which will raise unit mass of water one degree Fahrenheit on the mercury thermometer, and the unit of work being that spent in elevating unit mass one foot, the general relation between heat and work will be $H = W/772$, or $W = 772H$.

Unreduced value of J.

If the unit of heat be that required to raise unit mass of water one degree centigrade, the work equivalent will be the $\frac{9}{5}$ of 772, that is 1390, the unit of work being the same as before. But if the unit of work be that spent in raising unit mass one metre, the value of the mechanical equivalent will be 424. This is expressed by saying that the mechanical equivalent of heat is 424 gramme-metres, or the work spent in raising a weight of one gramme to a height of 424 metres will, if spent in friction, produce as much heat as will raise the temperature of one gramme of water one degree centigrade. Denoting the value of the mechanical equivalent by J in any system of units, we will have between the work spent and the heat produced the general equation—

$$W = JH.$$

The symbol J represents the number of units of work necessary to the generation of one unit of heat, when the work is all spent in generating heat. It ought to be remembered that in the experiments devised by Rumford and Joule, the work may not all be spent in generating heat. There may be electric or magnetic actions developed, or other actions may take place which we have as yet no means of detecting. If any such actions take place, the values of J derived by different methods and with different materials would not be expected to be equal, and if they are found to be equal it does not prove that such actions do not occur, but only that the ratio of the part of the work spent in producing heat to that spent in these other actions is the same in all the methods employed, or that the same definite fraction of the work is spent in all the methods in producing heat.

Joule was quite clear on the point that if the work is really all spent in producing heat, then with every form of apparatus we must obtain the same amount of heat for the expenditure of the same amount of work. He consequently determined the dynamical equivalent by the friction of other liquids than water, and by other methods than friction. The results of three series of experiments gave—

(1) Friction of water contained in a brass vessel with a brass paddle $J = 772 \cdot 695$.

(2) Friction of mercury contained in an iron vessel with iron paddle $J = 774 \cdot 083$.

(3) Friction of two iron rings rubbing against each other in mercury $J = 774 \cdot 987$.

In 1878 Joule repeated his experiments, and found the number 773·369 for the dynamical equivalent in the latitude of Manchester. This, reduced to the sea-level and the latitude of Greenwich, becomes 773·492, the unit of heat being that which raised the temperature of 1 lb. of water from 60° to 61° F., the weighing being made with brass weights when the barometer stood at 30 in. When the weighing is made in vacuo this becomes reduced to 772·55.

Later experiments on this subject have been carried out by Professor H. A. Rowland and several others. The experiments of Rowland are remarkable for their range and consistency, as well as for the skill and completeness with which they were executed. They were conducted at temperatures varying between 39°·1 F. and 96°·8 F. (a much wider range than that employed by Joule), and gave results varying from 774·7 to 778·3 on the mercurial thermometer, and from 775·9 to 783·4 on the air thermometer, the higher results being obtained at the lower temperatures (see further, Chap. VIII.).

Hence when the air thermometer is taken as the standard, Joule's results become augmented by nearly 1 per cent, and if the unit of heat be taken as the quantity required to raise the temperature of unit mass of water 1° at a temperature of 15° C. on the air thermometer, the foregoing results may be replaced by the numbers—

Corrected value at 15° C.

$$\begin{aligned} J &= 427 \text{ (gramme-metres degree C.)} \\ &= 778 \text{ (foot-pounds degree F.)} \\ &= 1400 \text{ (foot-pounds degree C.)} \end{aligned}$$

36. Transformation of Heat into Work.—We have seen how Rumford, Davy, and Joule proved that the work done by animals or falling weights may be converted into heat, and we shall now consider the converse operation—the transformation of heat into work, or the derivation of mechanical effect from thermal agencies.

This process is exhibited in the steam-engine and all other heat engines. Thus in the steam-engine fuel is consumed and heat generated in the furnace, and at the expense of this heat the engine is set in motion, and work is performed. The kinetic energy of the particles of a hot body, which, according to the dynamical theory, constitutes its heat, is thus transformed into the visible motion of the parts of the engine, and this in turn is transformed partly into external work, or mechanical effect, such as the raising of weights, or communicating motion to or altering the configuration or state of other bodies, or systems of bodies, and it is partly frittered down again into heat developed by the friction of the parts of the engine itself, or of other bodies which it may set in motion.

Thus in a locomotive the heat drawn from the furnace passes first into heat motion or energy of the particles of water and steam; this in turn passes into the motion of the machinery. All the visible

motion of the engine and its parts is thus derived from the invisible motions of the molecules of the water vapour, which in turn comes from the furnace, and this invisible motion or agitation of the molecules of a body we regard as the source of its sensible heat, and the performance of work by a heat engine we regard merely as a transformation of the kinetic energy of the particles of the hot body, or source of heat, into the visible energy of motion of large masses, or into that energy of position which we call potential energy. When a train starts from one level and comes to rest at some higher level, part of the energy derived from the furnace—that is, part of the heat motion—is spent in raising the mass of the train through the difference of level; this is stored-up energy (or potential), and may be recovered again as motion in allowing the train to fall to its original level. The remainder of the energy derived from the furnace passes first into energy of motion of the parts of the apparatus, and then into heat motions caused by friction developed in the rails, air, and parts of the train, and is then radiated into space. The engine thus acts the part of a still. The energy which first exists as heat motion in the furnace passes through the steam into visible motion of the machine, and then again takes the form of heat motion developed by friction.

If the engine be employed in merely producing motion in itself or other bodies without altering their relative positions or state, and if these motions finally subside through friction, as in the case of a train coming to rest at the same level as that from which it started, then on the whole there will be no external work done, there will be no mechanical advantage gained, and all the heat derived from the furnace will be frittered down, and reappear again as heat developed by the friction which brings the mass to rest. If, however, work has been done by the engine in raising its mass, or any other masses, to a higher level, an equivalent of the heat drawn from the furnace will disappear; this will have been used up in doing work, viz. the work necessary to raise the masses to the higher level; the remainder of the heat drawn from the furnace will reappear as heat developed by friction, so that the heat thus developed is not now the complete equivalent of that drawn from the furnace, but is less by an amount W/J where W is the work done in raising the masses.

The direct verification that heat disappears when work is done by a steam-engine was first experimentally demonstrated by Hirn in 1857, but as early as 1839 an essay was made by Séguin in the same direction.

Hirn's experiments.

Hirn actually measured in an ordinary working steam-engine the quantity of heat which was carried from the boiler in a given time, and also the quantity which reached the condenser during the same in-

terval. He also calculated the quantity lost by radiation and conduction over all parts of the machine, and found that when the engine was at work, turning other machinery, the difference between the quantity of heat which left the boiler and that which entered the condenser was much greater than when the engine performed no external work, and the steam merely passed through the engine from the boiler to the condenser.

Hirn also pushed the experimental inquiry further, and actually deduced a fair estimate of the dynamical equivalent of heat from his observations of the work done by the engine, and the quantity of heat used up in performing it. The work W performed in any time can be deduced from the area of the Watt's indicator diagram (see Art. 68), and the number of strokes of the piston. To determine the quantity of heat converted into work, the weight of water that passes from the boiler to the condenser must be estimated. Knowing the latent heat of vaporisation at the temperature of the boiler (see p. 313), the quantity of heat Q drawn from the boiler in any time becomes known. But this quantity is not all converted into work. Part of it q is carried into the condenser, and a part R is lost by radiation in the transit. Hence the quantity of heat converted into work is $Q - q - R$, and the value of J is found from the equation

$$W = J(Q - q - R).$$

By this means Hirn obtained the numbers 413 and 420·4 (grammemetres), which, considering the difficulty of the investigation, must be regarded as exceedingly good approximations.

37. The Two Laws of Thermodynamics—Meaning of the Term Law in Physical Science.—It has been shown that heat may be generated by the expenditure of work, and conversely that work may be performed by the expenditure of an equivalent quantity of heat. A certain equivalence has been shown, by the experiments of Joule, to exist between the work done and the heat generated (or spent) in such First law. cases, and this equivalence is known as the first law of thermodynamics. This law is algebraically stated in the equation

$$W = JH,$$

which means that when work is spent in generating heat, or heat spent in performing work, then J units of work are equivalent to one unit of heat.

In the general case a quantity of work W is spent in driving a machine, and a smaller quantity of work w is performed by the machine—for example, in raising weights or moving certain masses.

The balance $W-w$ is spent, partly at least, and perhaps wholly, in overcoming the friction of the parts of the machinery, and an equivalent quantity of heat is developed. It must not, however, be assumed that the heat thus developed is the complete equivalent of the difference $W-w$. Other processes besides the development of heat may be in operation. Electrical phenomena may occur, and generally do occur, when dissimilar substances rub together. Magnetic and electro-magnetic actions may also take place, and energy may be radiated into space or dissipated, during the motion or collision of masses, in modes which we are as yet unable to detect. The expenditure of the work in Joule's experiment may not be quite so simple as it appears at first sight, and until it is proved that in all such cases the work is wholly spent in producing heat, it is not clear that the value of J, determined by the friction of one pair of substances, should be the same as that determined in the same manner by another pair. That other actions do take place can scarcely be doubted, and perhaps it is to these that the differences in the determinations of J by different methods are to be partly attributed. The corrected equation would in this case be

$$W = JH + w,$$

where w represents the quantity of work spent in developing other phenomena hitherto unnoticed.

Second law.

The second law of thermodynamics was introduced by Clausius and Thomson, and these two laws form the basis of the modern science of thermodynamics. This law, as stated by Clausius, asserts that heat cannot be conveyed from one body to another at a higher temperature without the expenditure of work, or some equivalent process. Thus of a system of bodies at different temperatures any pair may be converted into a heat engine, that at the higher temperature acting as the source, or furnace, and the other playing the part of the condenser. When such an engine performs work the heat used up is always that of the source or body of highest temperature. A certain quantity of heat is drawn from the source, and part of this is converted into work, while the remainder passes into the condenser or body of lower temperature. If the process were reversed work would be spent in driving the engine, while a certain quantity of heat would be drawn from the condenser and a certain quantity would be restored to the source. Thus in the direct process heat is drawn from the warmer and given in part to the colder of two bodies, while external work is performed by the engine. In this process the tendency is to equilibrate the temperatures of the two bodies. In the reverse process, however, work is spent in driving the engine, while heat is drawn from the colder

and given to the warmer of the two bodies, and the tendency is to exaggerate their difference of temperature. It is from this point of view that Thomson regarded the matter, and proposed the principle that the method by which work is obtained from heat is by allowing it to pass from bodies of higher to bodies of lower temperature, or that work may be done by using up the heat of the warmer of two bodies but not by using the heat of the colder. In Thomson's statement the direct process of obtaining mechanical effect by thermal agencies is kept in view, and the impossibility of obtaining work by using up the heat of the coldest of a system of bodies is insisted on. In order that heat may be drawn from the coldest body the engine must be reversed, and work must be spent in effecting the process. This is the statement of Clausius, and the two are therefore equivalent.

An apparent violation of the second law of thermodynamics arising from our inability to deal with individual molecules has been ingeniously pointed out by Maxwell. The fuller consideration of this and other matters, together with the applications of the law, will be taken up again in the sequel (Chap. VIII.). At present it will only be necessary to call attention to the meaning of the word *law* in physics.

Physical laws.

A law is nothing more than a general conception which embraces a series of similarly-recurring natural phenomena. Thus the laws of reflection and refraction of light state general relations between the directions of two rays which under certain conditions are always found to hold. We have again the law of universal gravitation, and the law of the conservation of energy, and in chemistry the law of the conservation of matter. These laws may not be absolutely true, but they are stated as laws because, so far as our experience goes, they have not yet been found to be false, *i.e.* to lead to contradictory results. Such laws are not mere logical conceptions, but are evolved from the consideration of long series of observations, and are tested by repeated experiment under ever-varying circumstances. In proportion only as they are found to bear such tests does our confidence in their trustworthiness increase. They are for the most part working hypotheses of the greatest utility in systematising our knowledge and cataloguing facts. To find the true law of any class of phenomena requires a complete knowledge of the processes by which they are brought about; and before we can say that our knowledge of any one law of nature is complete we must have ascertained that it holds good without exception. Only so far as it has been tested can it be trusted, and when we say that any law is established by a series of experiments the *range* of the series must be stated, and it is only asserted that within this range the law is in accordance with the facts.

SECTION V

THE DYNAMICAL OR WAVE THEORY OF HEAT

38. Antiquity of the Dynamical Theory.—Having learned that heat may be generated by the expenditure of work, and *vice versâ*, we shall now consider the theory which has been founded on these facts.

The first notions of the dynamical theory of heat date from such a remote epoch that their origin cannot be attributed with precision to any single person or period. Thus some of the Greek philosophers, from mere observation of the destructive effects of heat, considered it as a movement of the ultimate particles of matter. So also at the time of the scientific renaissance inaugurated by Bacon, and continued by Descartes, we find the claims of the dynamical theory freely advocated. These statements of the doctrine, however, can only be regarded as more or less acute speculations, as no sure basis for the theory was laid till Rumford and Davy executed their experiments, nor indeed was the theory generally accepted until a considerably later period. The calorist, in fact, had not become extinct in the middle of the nineteenth century! While the majority of scientists were convinced that light was due to wave motion in the ether, they still adhered with the greatest pertinacity to their heat fluid or caloric.

39. The Ether.—Although we are forced to regard space itself as unlimited, yet there is no mental necessity compelling us to regard it either as filled throughout, or in part, with a medium, or as entirely empty. When, however, we endeavour to explain the phenomena of heat and light we are forced to the conclusion that all space, at least as far as the farthest visible star, is filled with a fundamental medium called the ether. This hypothesis is forced upon us by the fact that heat and light travel through space with a definite velocity, and we find it impossible to conceive of more than two methods by which an influence, travelling in time, may be propagated from one body to another situated at a distance.

Take, for example, the case of two ships at sea. One of these may

Two methods of explanation.

disturb the other in either of two ways—either by firing bullets against it or by exciting waves in the water (medium between them) which, diverging from the centre of disturbance, break upon the other ship and disturb it. In the first case one emits a substance which impinges against the other, and in the second it is the source of a disturbance which travels through a medium existing between the two. The former method is the basis of the emission theories of heat and light, and on the latter is founded the wave theory. According to the emission theory, a hot or luminous body emits a fluid or a shower of fine particles, travelling through space with the velocity of light (300,000,000 metres per second). This theory has been altogether abandoned, and the supposition that light and heat are due to wave motion in a medium filling all space has been universally adopted. The medium is of course hypothetical, in so far as what we term the *direct* evidence of our senses is concerned. It is not visible or tangible except as the vehicle of all our light and heat; yet its existence is advocated by the phenomena of electricity and magnetism, and, in fact, by all the operations of nature. When we speak of the direct evidence of our senses, how do we circumscribe the term? what exactly do we mean? what fixed line of demarcation have we to tell us where this evidence begins and where it ceases?

The notion of such a medium is neither new nor fanciful, nor is it to be regarded as a vague speculation on the part of scientists. The hypothesis has been admitted on accumulated evidence, and in consequence of the demand for a rational and consistent explanation of all the phenomena of nature. It is certainly as easy to conceive of space as filled with a medium, capable of carrying energy from one region to another, as to believe that the interstellar spaces are entirely empty; and if the question be impartially considered it will perhaps be conceded that we have really as much reason for believing in the existence of a universal ether as in that of anything else.[1]

Postulates.

It is to be remembered, however, that we do not postulate density, or compressibility, or molecular structure, or necessarily any property of matter, for this ether, except that it can contain and propagate energy. It is merely assumed as a fundamental medium, by means of which the properties of all substances, and all the phenomena of nature, are to be explained. It is certainly unscientific to postulate elasticity and density, or any structure, for this medium, if by means of it we are to account for the elasticity, density, and structure of

[1] The ancients certainly appear to have had no difficulty in admitting the simultaneous existence of several ethers and imponderable fluids, and at the present time the vast majority of people think of electricity as a fluid, or two fluids!

matter. Such a procedure does not even push the inquiry one stage farther back.

40. Heat and Light Reducible to the same Agency.—The idea that heat is ultimately due to a motion of some sort has been long entertained. By friction and collision the sensible motion of bodies disappears and heat is generated. The supposition has been that the motion in such cases is not really lost, but is merely transferred from the body as a whole to its individual particles. Thus when a moving body is brought to rest by friction, or collision, the energy of the original visible motion of the body is not annihilated, but passes over into the invisible atoms of the substances taking part in the friction or collision.

Now we have evidence in favour of the supposition that light is due to wave motion in the ether, and we have exactly the same evidence in favour of the same supposition with regard to heat. Radiant heat (for example the heat emitted by hot-water pipes or a blackened stove) and light behave in exactly the same way in a variety of experiments—in fact the only difference that can be detected is that light, as well as possessing all the characteristic qualities of the radiant heat, is also able to affect the sense of sight.

Heat then, like light, is supposed to be due to wave motion in the ether.[1] We say that the molecules of a hot body are in a state of very rapid vibration, or are the centres of rapid periodic disturbances of

[1] Among the contemporaries of Rumford and Davy, Dr. Thomas Young seems to have been the only man who comprehended the full bearing of their experiments. He called in question the principle assumed by the calorists, that the heat absorbed in any process is precisely the same as that evolved when the body passes back again to its initial condition, and points out that this assumption had not been proved in a single case ("Lecture on the Nature of Heat"). That Young had thoroughly grasped the idea of the wave theory is proved by the following passage:—"If heat be not a substance it must be a quality, and this quality can only be motion. It was Newton's opinion that heat consists in a minute vibratory motion of the particles of bodies, and that this motion is communicated through an apparent vacuum by the undulations of an elastic medium, which is also concerned in the phenomena of light. If the arguments which have been lately advanced in favour of the undulatory nature of light be deemed valid, there will be still stronger reasons for admitting this doctrine respecting heat, and it will only be necessary to suppose the vibrations and undulations principally constituting it to be larger and stronger than those of light, while at the same time the smaller vibrations of light, and even the blackening rays, derived from still more minute vibrations, may perhaps, when sufficiently condensed, concur in producing the effects of heat. These effects, beginning from the blackening rays, which are invisible, are a little more perceptible in the violet, which still possess but a faint illuminating power; the yellow-green afford the most light; the red give less light, but much more heat; while the still larger and less frequent vibrations, which have no effect on the sense of sight, may be supposed to give rise to the least refrangible rays, and to constitute invisible heat."

some sort, that they thus excite waves in the ambient ether, that these waves travel through the ether between us and the body with the velocity of light, and that when they fall upon us they are more or less absorbed by, and cause corresponding motions in, the molecules of our bodies, and thus arises the feeling of hotness. The sense of heat in us is thus excited by the ethereal waves diverging from the hot body, just as the eye is excited by the waves diverging from a luminous body, or as the ear, in an analogous manner, is affected by the aerial waves originated by a sounding body.

The question now arises, Are there two distinct sets of waves in the ether? Are there heat waves and light waves, or are these waves of the same nature and type? That a light wave also possesses heating power at once leads us to suspect that there is no essential difference in character between the wave motion which affects our sense of heat and that which affects our sense of vision. To explain how this may be we revert to the more easily comprehended case of sound.

Effect of frequency.

If a sounding bell vibrates one hundred times per second it generates waves in the air which are about 11 feet in length, and if it vibrates eleven hundred times per second the corresponding waves are about 1 foot long, while fifty vibrations per second will give rise to waves about 7 yards in length, and so on. The impression upon the ear depends on the number of waves which fall upon it per second—that is, upon the rate of vibration of the sounding body, and as a consequence we derive the idea of pitch. That is, we say a note is high or low according as the number of vibrations per second is comparatively large or small. Further, the range of the ear is limited, and the rate of vibration may be so high that the ear fails to respond to the demand upon it, and the rate of vibration may, on the other hand, be so low as to cause no distinct impression. In other words, the aerial waves may be too short or too long to cause the impression of sound.[1] There are certain limits of length between which the waves must lie—from about 12 or 13 yards to about $\frac{1}{3}$ of an inch. These limits are determined by the construction and constitution of the ear, and vary slightly from individual to individual. The very long waves and the very short waves which do not affect the ear are, however, waves of exactly the same character as those which cause the impression of sound, the only difference is one of

[1] The rapidity of vibration or frequency is the main point to be kept in view rather than the length of the wave, and in what follows, a short wave is to be taken as meaning one of high rate of vibration, while a long wave is one of low rate. For the same rate of vibration the actual length of the wave will depend upon the nature of the medium.

rapidity. The fault lies with the ear and not with the waves. We do not say that there are two distinct classes of aerial waves, those which give rise to sound and those which do not. We prefer to look upon all the waves as of the same class—that is, the physical process in action during the propagation of all is the same. The difference is merely one of rapidity, and, as the range of the ear is limited, it cannot meet the demands upon it in both directions to an unlimited extent.

In the same manner every body in space is regarded as a source of incessant ethereal commotion. Every molecule of matter is in vibration, and generates waves in the ether. The clouds may shut off the light and heat of the sun, but they are warm bodies themselves, and radiate waves of heat. The earth itself is warm, and on the coldest night the dark space embraced by its shadow is traversed with incessant streams of radiated waves. We are thus bathed day and night in the midst of never-ceasing change. The ether is never still.

It is, however, to be distinctly remembered that we do not make any assumption as to the nature of the vibration or the process going on in the ether. We merely call it a vibration, because we believe it to be a periodic variation of some sort. This never-ending tremor affects us in two distinct ways. To it we owe the sensation of vision as well as that of heat. If an ethereal wave lies between certain limits of frequency it affects the eye, and we call it light. Such a wave falling upon our bodies may also set up commotions among our molecules, and give rise to the feeling of warmth. The same wave may thus cause two distinct impressions, that of light and also that of heat, just as if a sound wave could not only affect the ear but could also cause our bodies to tingle and develop a sensation of warmth. Thus while we have only one sense to tell us directly that the air is vibrating, we have two by which we can examine the ether. In this aspect, then, the sense of heat may be regarded as an extension of the sense of sight (see Art. 13).

41. Existence of Waves beyond the Limits of the Senses.—The eye, like the ear, is, however, limited in range. An ethereal wave may be either too slow or too quick to affect it. Outside these limits waves of any power might fall upon us, and yet we would be enveloped in perpetual night. Our sense of heat would, however, come to the rescue. Waves which are too slow to affect the eye can warm our bodies. Thus these two senses overlap and extend each other. The waves, however, which most powerfully affect the eye are not generally those which most excite the sense of heat. While some

waves are of such a length that they can be easily detected by either sense, still some are so long that the eye fails to cope with them, yet they are easily responded to by the sense of heat; and, on the other hand, some are so short that although they may affect the eye yet they are with difficulty, if at all, detected by the sense of heat.

We are now left with those waves which undoubtedly exist in myriads, and which are too short or too long to be detected by either the sense of sight or the sense of heat. By means of our unaided senses such waves might fall upon us for all time, and still we could never become aware of their presence. An ether might exist and be continually troubled by such waves, and yet we could have no direct evidence of their existence or of the medium which carried them. The suggestion of such a medium by any one would probably be looked upon as strong evidence of insanity. Even with the double evidence of our senses which we now have in favour of a space-filling ether, there are many who would rather doubt such evidence than believe in a thing which they cannot taste or smell (for according to our theory they can both see and feel it, and are in and of it). However, considering the medium as only hypothetical, the fact that it might certainly exist and fill important functions in the life of the universe and still never be detected or suspected by us is a strong reason why the postulation of such a medium for the explanation of natural phenomena should not be branded as irrational or unphilosophic.

The ingenuity of man has not allowed these long waves, nor even the very short waves, to escape. Those which are too short to be directly detected by the eye can be placed in evidence by means of their chemical action, while those which are too long to affect our sense of heat (it is only waves in the neighbourhood of $\frac{1}{2000}$ part of a millimetre that act directly on our senses) have been recently subjected to the power of man by the celebrated experiments of Professor Hertz. Previous to 1889 we were confined in our observations to waves about $\frac{1}{30000}$ part of an inch in length, now we can work with ether waves a foot or a yard or a mile long if desired.[1]

42. Common Theory of Light and Heat.—We thus have a common theory for heat and light. It is the theory of waves in the ether. The sensations of warmth and vision arise from the effects of the same agent. We have two senses for detecting the same ethereal disturbance. Hence whatever theory we form to explain the phenomena of light must also satisfactorily explain the phenomena of heat. In the study of light, however, we are concerned chiefly with the laws

[1] See the author's *Theory of Light*, chap. xxi.

of propagation of the waves through the free ether or through transparent matter, and with the interference, or mutual action, of various sets of waves passing simultaneously through the same portion of space. In the study of heat, on the other hand, we are concerned largely with the effects produced by these waves on matter. Here we investigate the modifications and mechanical actions experienced by matter when ethereal waves fall upon it or are emitted by it—that is, in other words, as it receives or emits heat. It is more the study of the matter, or of the effects of heat upon it, than of the radiation or nature of the wave motion in the ether, to which we attribute the phenomena of heat and light. Hence before we proceed to the study of the effects of heat it may be of advantage to glance at some considerations in relation to matter and motion, and the ether as the vehicle of energy, for before any theory of heat can be worked out in full detail some satisfactory theory of matter must be first formulated, and this appears to be a task of no ordinary difficulty.

We shall, therefore, consider briefly the evidence we have regarding the structure of matter and the causes which determine its composition and physical state. A full knowledge of the ultimate constitution of matter may possibly lie beyond the grasp of the human intellect, for this can only be traced with certainty as far as our senses, combined with physical apparatus, enable us to observe it. The essential differences, however, between the three typical forms —solids, liquids, and gases—and their modes of interaction, form a legitimate subject of inquiry.

SECTION VI

ON MATTER

43. Definitions.—Various, and very diverse, definitions of the term matter have been proposed from time to time. The experimental physicist, however, uses the word merely to denote the substance or stuff contained in the objects around him, and which constitute what is termed the external or material universe. These objects we recognise and distinguish by means of their properties—that is, by the impressions, direct or indirect, which they make on our organs of sense, and by means of which we perceive their presence and consequently say they exist. Two general properties have been usually attributed to matter, namely, *extension* and *impenetrability*, the former term being used to signify that any portion of matter occupies space, or has volume, and the latter to denote that two bodies, or portions of matter, cannot occupy the same portion of space at the same time.

The term impenetrability thus appears to mean pretty much the same thing as extension, for if we say a body occupies a certain space, we ought to mean that it occupies that space to the exclusion of all other bodies. So that in addition to referring to no new property, and being therefore unnecessary, the name seems to be ill chosen, as it is undoubtedly misleading in its signification.

We distinguish different kinds of matter by such properties as compressibility, greater or less rigidity, colour, taste, smell, but the one property which characterises all forms of matter, as we know it, is *weight*. We measure matter by weight, and we say that two bodies of equal weight have equal masses—that is, contain equal quantities of matter. The term "conservation of matter" might, therefore, with advantage be replaced by the term "*conservation of weight*," as it would keep the mind in closer touch with the property that really is conserved throughout chemical processes, namely weight. Thus there is no mental necessity compelling us to believe that the weight of two

or more atoms in chemical combination should be the same as the sum of their separate weights before combination, even though the quantity of matter (measured in the same way) remained the same as before. Thus if matter be regarded as an objective reality independent of man and his ideas, then we could easily imagine that matter should remain permanent in quantity throughout any chemical change, and yet the weight in the same case might be very different at the end of the reaction from that at the beginning. It is, therefore, better to adhere strictly to the main fact, namely, that the weight is conserved so far as our experience has yet gone.

The property of extension, however, does not sufficiently circumscribe the term matter for our purpose, for this property belongs to anything conceivable by the human mind as existing in space. We do not wish to call the ether matter, or if we adopted the fluid theory of heat or electricity, or the corpuscular theory of light, we should avoid calling these media matter, for they have all been supposed to be devoid of weight, which is the characteristic of all matter as we know it. We might speak of ether, or caloric, or electricity, as fluids or fluid media, or simply as media, but never as matter. It must now be clear that when we speak of matter we use the term for the sake of convenience to denote that stuff which constitutes the bodies around us, and that the property common to all kinds of matter, as we know it, is weight.

What we constantly *observe*, however, is change; and in matter we observe both change of quality or state, and change of position or motion. Thus wine when exposed to the air turns into vinegar, and water when heated turns into vapour. The former is a change in quality and is termed a *chemical* change or process, while the latter is a change of the state of aggregation of the matter and is referred to shortly as a change of state. The motions of bodies we say are originated or caused by *force*, and in the case of a body of definite mass the measure of the force is taken as the mass multiplied by the rate of change of velocity. In this sense then should the word be employed, and in this sense only has it any definite meaning. Since velocity and change of velocity have magnitude and direction (estimated according to some definitely arranged plan), forces possess also both magnitude and direction.

44. Divisibility of Matter.—Much futile discussion has been engaged in by metaphysicians and physicists as to the infinite divisibility of matter. A block of wood may be split in two by a hatchet, and each of these portions may be again divided, and so on. The question then arises, Can this process of subdivision be carried

on indefinitely? Divisibility in the abstract can certainly be carried on indefinitely, for here it only depends on the imagination; but in practice it is quite a different question. If any body can be divided into two portions it is a matter to be tested by experiment alone if each of these portions can be divided into two others, and so on indefinitely. The question of the *infinite* divisibility of matter is, however, beyond the scope of experiment, since the infinite, from the very meaning of the word, cannot be the subject of experience. The question is therefore an objectless one for experimental science.

If by experiment, however, it were found that the process of division could not be pushed beyond a certain limit, that we finally came to parts which we could not further break up, we still would not be justified in saying that further division is impossible, but should rest satisfied with stating that we did not yet possess the means of pushing the division any further.

45. Antiquity of the Idea of Atoms and Molecules.—The idea that all bodies are composed of a multitude of very small particles seems to have been entertained since the earliest times of civilisation. The *hard* atom was conceived 2400 years ago by the Greek philosophers Democritus and Leucippus, and was subsequently glorified in the poetry of Lucretius. An argument urged by the latter in favour of the hypothesis is the facility with which it lends itself to the explanation of the mobility of fluids such as air and water. This arises, according to the poet, because there are vacant spaces between the perfectly solid particles, and hence, although the particles are hard, yet the substance as a whole may be soft and yielding.

The idea of a perfectly hard atom seems to be refuted by all those modern researches, such as spectroscopic work, which lead us to reflect on the molecular structure of matter. The behaviour of matter in regard to radiant heat and light leads us irresistibly to conclude that an atom is not simply a hard, structureless particle, but that it is a more or less complicated system capable of internal vibrations of several distinct periods.

The atomic theory, however, only acquired a definite form at the beginning of this century, when it was revived by Dalton to explain the fact that in chemical combinations the elements unite in certain definite proportions. Since that time the hypothesis has grown in strength, and has been a fruitful instrument of progress in many branches of physical science, so that it now claims the rank of a well-tested theory.

46. Value of a Theory.—Such a theory, however, claims not the truth of an abstract law. The human mind deals much less easily

with abstract truths by themselves than by aid of well-conceived analogies and illustrative imagery. The value of any hypothesis depends upon its convenience in systematising observed facts, and to the extent to which it embraces all known phenomena must its utility be estimated. Such an hypothesis cannot be proved. It may be true, but it must, nevertheless, be regarded merely as a tool to be used for the sake of convenience as long as it is consistent with observation, and which must be rejected, or modified to suit our wants, when found to be no longer applicable. A well-chosen hypothesis not only concatenates the observed facts, and gives a clear and connected idea of the general laws to which they are subject, but may often lead to the discovery of new relations, and thus place in our hands the means of anticipating phenomena previously unobserved. The process of scientific inquiry may be thus advanced from the stage of blind groping to that of well-planned and conscious investigation.

47. Molecules considered as Groups of Atoms.—According to the molecular theory all bodies consist of very small parts termed molecules. Every molecule is supposed to be similar to every other molecule of the same substance, and to possess all the mass properties of the substance. In other words, it is the smallest part of the body which can be separated from it and still possess all the characteristics which distinguish the substance. The necessity of this limitation arises from the fact that substances which are apparently homogeneous can be decomposed into two or more other substances which are very dissimilar in their properties. Thus water can be decomposed into hydrogen and oxygen, the volume of the former being twice that of the latter. For this reason a molecule of water is said to consist of two atoms of hydrogen united to (or in chemical union with) one atom of oxygen. It must, however, be admitted that we have no right to assert that two atoms of hydrogen united in this way to one atom of oxygen—that is, a molecule of water—would, if we could deal with it, possess all the mass properties of water. Any portion of a substance that we can subject to experiment contains an enormous number of molecules, and its properties may be, and probably are, very different from those of a single molecule. The chemical definitions, therefore, require modification.

It is also found that such substances as hydrogen and oxygen cannot be further decomposed by any process at our command, and they are consequently said to be simple substances. An atom is the smallest portion of a simple substance which can enter into chemical combination. A molecule, on the other hand, may consist of two or more atoms associated together in a manner which we do not

as yet understand, and to denote this manner of association we say they are in chemical union. A molecule of a compound substance is thus a little society of atoms of what we call the elementary substances. Thus if we suppose the solar system to dwindle down till the masses forming it attained the size of atoms, then the whole system thus associated might be taken to represent what we call a molecule, the different planets and their satellites forming its constituent atoms.

48. Evidence in Favour of the Atomic Theory.—The atomic theory involves the supposition that there is a practical limit to the divisibility of matter. In fact, it is only on this supposition that any definite meaning can be attached to the existence of elements in chemical combination according to Dalton's law of multiple proportions. An atom as a whole enters into or passes out of chemical combination; a portion of it cannot be removed from a molecule leaving the rest in combination, and this is what the name signifies.

All chemical experience harmonises with the atomic theory, and finds in it an easy and intelligible mode of expression. The hypothesis is also strongly corroborated by spectroscopic researches, and by observations in the other domains of physical science; yet, as to the ultimate nature of matter, and as to the question whether in going on dividing a portion of matter we should finally arrive at an atom, or portion which could not be further divided, man is still quite as ignorant as he was in the days of Lucretius. The solution of this problem appears to recede from our grasp as fast as we approach it, and this, perhaps, is as yet a matter of indifference in chemical investigation.

49. Idea of a Fundamental Substance—The Protyle Theory.—Any substance, such as oxygen or hydrogen, which cannot be further decomposed, is called an element or simple substance. It must be carefully remembered, however, that an element in the chemical sense is an undecomposed, not necessarily an undecomposable, substance. Attempts to draw general conclusions as to the constitution of the various elementary substances, from the values of their atomic weights, have been made in two directions. The first line, started by Prout in 1815, was based upon the philosophic assumption of a fundamental substance, or "protyle." This substance was supposed to be hydrogen,[1]

[1] Some remarkable observations on gases sealed in "vacuum tubes" were communicated in 1889 to the British Association by the late Professor Piazzi-Smyth, from which it would appear that other gases and elementary substances gradually decompose into hydrogen. If this be true, direct support is given to the supposition that all the so-called elementary substances are merely compounds of hydrogen.

and all the other elementary substances were supposed to be made up of it, so that if weight be conserved throughout chemical combination, or such combination as would yield the various elements out of hydrogen, then the atomic weights of all the elements, and in fact of all substances, simple or compound, should be multiples of that of hydrogen. In other words, if the weight of an atom of hydrogen be taken as unit of weight, then the weight of an atom of any other element, or of a molecule of any chemical compound, should be expressible as a whole number, provided the weight of a molecule be equal to the sum of the weights of its constituent atoms.

The test of the applicability of such a theory will depend upon the accuracy of the determination of the atomic weights of the elements, and in the opinion of J. S. Stas, the accuracy of whose work far surpassed that of his master Dumas, the hypothesis of Prout is inadmissible. The atomic weights in many cases differ from those required by the theory by quantities much larger than the probable errors of experiment. There is, however, a surprising approximation to the multiples of hydrogen in the atomic weights of many elements, and Dumas devoted himself to showing that although the atomic weights of all the elements could not be exactly expressed as multiples of hydrogen, still they all could be expressed very approximately as multiples of half the weight of a hydrogen atom. Afterwards, however, he was forced to adopt the quarter hydrogen atom as the basis of all the other elements, so that the whole subject here loses all practical interest, for it is evident that by taking a sufficiently low limit of weight the approximation could be carried to any degree of closeness. In spite of the unsurpassed work of Stas, the question is constantly being revived by astute thinkers. Certainly the hypothesis

Various elementary substances were sealed up in vacuum tubes, and exhibited their characteristic spectra. After some time, however, these spectra began to grow fainter and less characteristic, and hydrogen lines began to appear. "Thus, in a chlorine tube of which it was printed in 1880 that it was then showing its chlorine lines, though fainter, after two years' use, while carbon-bands and hydrogen-bands had begun to appear, yet now (in 1889) has nothing but hydrogen lines, and in great brilliancy, to show."

"Again, an iodine tube which had a comparatively large quantity of solid iodine granules introduced into, and sealed up in, its interior eleven years ago, and showed then a splendid spectrum of 148 measured iodine lines, extending discontinuously from red to violet, and had nothing else save these very faint, puny images of the three principal lines of hydrogen—this tube, in 1889, has not a single iodine line now left; but its spectrum, which is brighter than ever, is composed of nothing but hydrogen lines, so that the once solid iodine granules would seem to be partly changed into hydrogen, and partly deposited on the inside of the tube as a yellow haze, besides leaving a trifle of loose dust."—Extract from *Nature*, 10th October 1889, p. 584.

is very attractive, but so far it cannot be regarded as resting on any sufficiently established basis.

50. The Periodic System.—The second line of consideration, introduced in 1864 by Newlands in England, and Lothar Meyer in Germany, might be termed the periodic system. In the hands of Lothar Meyer and Mendelejeff it has yielded a considerable harvest, and they have shown that in a fairly general way the properties of the elementary substances are periodic functions of their atomic weights. Thus if all the elements be arranged in the order of their atomic weights their chemical properties will vary from member to member till a certain number of elements have been passed, and then these properties, or very similar ones, will be repeated again in order as we pass up the series of elements. This system is by no means perfect. Many incongruities still remain to be eliminated by new facts, or fresh considerations, and so far it can only be regarded as the commencement of what promises to be a fruitful method of investigation.

51. Continuity Possible.—The supposition of atoms and molecules is, however, by no means absolutely necessary. Matter might also be regarded as continuous and structureless, not composed of discrete particles, but completely filling the space enclosed by the surface of the body. It is difficult, from this point of view, to explain compressibility, unless we postulate it as a primary quality of every element of matter, yet the theory need not be discarded at once on this account. Our powers of forming conceptions are limited by our experience, and to say that a supposition is inconceivable is merely to assert that it has not yet come within the bounds of our experience. Every explanation in physical science is but a reduction of a complex problem to its simpler elements, and there is probably a limit to such reduction beyond which the mind of man may never pass. Our explanations, in all cases, are made in terms of ideas which arise out of our experience. Beyond this we cannot go, but we attempt to fathom the unknown by means of analogies derived from the known.

52. Heterogeneity Possible.—Chemical combination might result from the mixture of different substances which penetrate each other so intimately that we cannot find in the compound the properties of any of the separate substances of which it is composed. The smallest portion which we can examine is apparently homogeneous with the whole mass. The mass, however, may still be intensely heterogeneous, and in fact such heterogeneity is pointed to in apparently homogeneous bodies, such as water and mercury, by different lines of reasoning based on experimental facts. Lord Kelvin[1] has shown that

[1] W. Thomson, *Proc. Roy. Soc.*, Edinburgh, 1862.

with such a constitution of matter gravitation alone would sufficiently explain the greater part of the phenomena which have been ascribed to the so-called molecular forces. That such heterogeneity might actually exist in the apparently most homogeneous substances and still escape notice is clear, for its detection will depend on our powers of observation. Thus, if we consider a cubic mile of pudding-stone forming a practically continuous mass, made up of blocks of various sorts of stones varying in volume from a cubic foot to a cubic inch, then one cubic foot of such a conglomerate might differ entirely from another cubic foot, and we would say the mass was intensely heterogeneous. If, however, we suppose the whole mass to be reduced according to a uniform scale, so that the cubic mile becomes a cubic foot, the heterogeneity will now fairly escape observation, and we should say that of such a mass any cubic inch was the same as any other cubic inch. In fact, we should say the mass was homogeneous. Thus, in a liquid the molecules may be clustered at some points and uniformly distributed at others, so that at some points the molecular aggregation may approximate to that of the solid state, while at others it may resemble that belonging to the vapour.

This idea of ultimate heterogeneity in masses which are apparently homogeneous will be found very useful in dealing with some phenomena which at first sight appear difficult to explain, such, for example, as variations of specific or latent heat. Thus in the fluid state the molecules at some points may be arranged in that condition which characterises the solid state. It is not at all likely that a system of molecules which mutually attract each other would travel for ever singly (as they are ordinarily supposed to do in a permanent gas) as if they were a system of hard spheres. It is much more likely that at some points they will get into clusters, so that here and there in the gaseous mass an element of the substance partakes more of the properties of a liquid than of a gas, and as the gas approaches its condensing point more closely it is likely that these clusters rapidly increase in number until condensation sets in. So also when a liquid approaches the freezing point, the state of aggregation which appertains to the solid state may be regarded as coming more and more into prominence until solidification actually sets in. The whole idea, then, comes to this, that we shall be probably near the truth in regarding as ordinary gas a mixture of what we call a perfect gas with the liquid, and a liquid may in the same way contain a portion of the solid in solution.

53. Three States of Matter — Molecular Theory.—The three states of matter—viz. solid, liquid, and gas—must now be considered

with reference to the molecular theory. In general, any substance may take each of the three states—the state in which it happens to exist being determined by its temperature and pressure. Thus, water substance at the ordinary atmospheric pressure may exist either as solid ice, liquid water, or be altogether converted into vapour, according to the temperature.

To explain this, the theory supposes that the molecules of every body are in a state of perpetual agitation, and this may consist in the motion of the molecule as a whole, or as a vibration or rotation of its constituent parts, or both. This molecular motion is supposed to depend upon the temperature; the hotter a body is, the greater the intensity of its molecular agitation. In a solid the molecules are supposed to oscillate round mean positions. Each is confined to a very small space, which it never leaves. As the temperature rises the molecular agitation increases, and at length becomes so violent that the molecules break away from their imprisonment and wander about indiscriminately amongst each other. In this state the substance is said to be in the liquid form.

In a liquid, then, the molecules as well as being in a state of vibration have also a motion of translation whereby they continually move in and out amongst each other, so that any molecule in one part can pay a visit to another in any other part of the liquid. Such a visit, however, is quite accidental. Each molecule is so jostled by the others in its wanderings that its path is almost entirely fortuitous. In order to endow the molecules with this extra motion, and also to overcome the forces which held the molecules confined in the solid state, work must be done, and this work is the equivalent of what is known as the latent heat of fusion. This continual interchange of position and gliding through each other of the molecules of a liquid is suggested by the phenomenon of diffusion, which takes place even in opposition to the force of gravity.

If we now consider a liquid to be gradually heated the molecular energy will increase, and when a molecule approaches the surface it may possess a velocity sufficient to project it completely from the liquid into the space above against the attraction of the neighbouring molecules in the surface layer. There will thus be a continuous stream of projected molecules leaving the liquid, and this is what we know as evaporation, and when the molecules all attain velocities sufficient to carry them through the surface layer, the liquid will all pass into the state of vapour or become a gas.

The essential difference between a liquid and a gas according to our theory is, that while in a liquid the molecules move about amongst

each other, each can travel no appreciable distance before it encounters another, and has its direction of motion altered by impact or mutual influence. In a liquid there is nothing of the nature of a free path; each molecule is constantly under the influence of its neighbours. In the case of a gas, however, each molecule between two consecutive collisions is free from the influence of the others.[1] There is a free path, and this path is rectilinear but very short. In the passage from the liquid to the gaseous state, the molecules must be separated from each other in opposition to their mutual attraction, and the work thus spent represents part, at least, of what is known as the latent heat of vaporisation.

54. Encounter and Free Path.—When two approaching molecules come within a certain limiting distance of each other, their relative velocity in the direction of the line joining their centres is supposed to diminish gradually, and become finally reversed. This mutual action is referred to as an *encounter* between two molecules, and in a permanent gas the time spent during an encounter must be much less than that occupied in the free path. As the density of a gas increases the length of the free path diminishes, and the encounters become more frequent. The proportion of time spent in collision becomes comparable with that of free motion, and the properties of the substance become considerably modified by the mutual influence of the molecules on each other. The effect of compression is to bring the molecules more within the sphere of each other's attraction, so that the substance gradually loses the characteristic properties of a perfect gas and acquires gradually the properties appertaining to the liquid state. In liquids there is no free path. The molecules are continually within the sphere of each other's attraction, and the behaviour of the substance with regard to pressure and temperature will be determined by the nature of the molecules and their mutual action. On the other hand, the mutual influence of the molecules is practically negligible in gases, and the behaviour of such substances with respect to pressure and temperature will, within certain limits, be independent of the nature of the molecular attraction, and the law connecting volume, pressure, and temperature will be the same for all gases.[2] It ought to be kept in mind, however, that when two molecules approach each other the encounter may not always be accompanied by a rebound, for the two may start rotating about

[1] The reasons for this supposition will be given afterwards, see Art. 218.

[2] Professor Crookes regards the ultra-gaseous condition in which the molecules are so far apart that collision is rare as a *fourth* state of matter ("Radiant State of Matter," *Proc. Roy. Soc.* vol. xxx. p. 469, 1880).

each other, and thus form the nucleus of condensation which leads to the heterogeneity spoken of in Art. 52.

55. The Dynamical Theory of Gases.—In order to account for the pressure of gases against the walls of the enclosing vessel, as well as their power of expanding to fill any space, their molecules were endowed by many philosophers with mutually repelling forces.[1] The idea that the molecules of a gas repel each other does not seem to be yet quite extinct, although it was shown by Daniel Bernoulli[2] as early as 1738 that the pressure and expansive power of gases could be satisfactorily explained by the supposition of molecular motion.

Let us, for the sake of clearness, consider the molecules of a gas as small equal masses, and let us inquire into the effect of a number of such molecules when enclosed in a vessel, and each in rapid motion. Let the vessel be a horizontal tube closed at one end, and having a movable piston fitting into the other, so as to slide freely in it. We shall consider the bombardment of the molecules against the piston. Each molecule as it strikes the piston communicates a certain impulse to it which would set it in motion outwards if not held at rest. Here, then, at once we find that a certain force will be necessary to hold the piston in position, or, in other words, the enclosed gas exerts a pressure in virtue of the motion of its molecules. The force necessary to hold the piston in position will depend on the number of molecules which strike it per second, and for molecules of a given kind moving with a given velocity this will be proportional to the number of molecules per unit volume, that is, to the density of the gas. The pressure then will be proportional to the density, that is, inversely as the volume when the mass is given. If the temperature of a gas depends only on the motion of its molecules, it will follow, then, that at constant temperature the product of the volume and pressure will be constant. Thus we have deduced Boyle's law as an immediate consequence of the dynamical theory.

We shall now examine the matter a little more closely. If a molecule of mass m approaches a wall with a velocity u, and rebounds with

[1] The assumption of such a mutual repulsion between the molecules of a gas is contrary to all experience, except the term be restricted to such forces as those which come into operation during impact and rebound. For if the molecules repelled each other, their kinetic energies would increase as their distances from each other increased, that is as the volume of the gas increases. Consequently, if a gas expanded without doing external work, its temperature would rise, that is if the temperature is determined by the energy of motion of the molecules.

[2] Bernoulli, *Hydrodynamica*, Strasbourg, 1738.

the same velocity, the momentum or impulse given to the wall by the impact will be twice the momentum of the molecule, that is

$$2mu.$$

For simplicity let us consider a single molecule moving perpendicularly to a pair of opposite sides of a cubical box of unit volume. If the molecule moves backwards and forwards with velocity u impinging on the two sides alternately, it will strike each side $\frac{1}{2}u$ times per second (since the space traversed between two consecutive impacts on the same wall is twice the edge of the cube or two units of length), hence the impulsive pressure caused by a single molecule will be

$$2mu \times \frac{u}{2} = mu^2,$$

and if n molecules be enclosed the pressure will be the sum of the partial pressures due to the individual molecules (that is, if they are so sparsely distributed that their mutual influence may be neglected), and the pressure will be

$$p = \Sigma mu^2 = m\Sigma u^2.$$

If, however, $\bar{u}^2$ be taken to represent the mean of all the values of u^2 for the various molecules, then if there be n molecules in the unit volume we shall have $n\bar{u}^2 = \Sigma u^2$, and

$$p = mn\bar{u}^2.$$

Now, in the general case a molecule may be moving in any direction with a velocity V, the rectangular components of which perpendicular to the faces of the cube are u, u', u'', so that

$$V^2 = u^2 + u'^2 + u''^2,$$

and if $\overline{V}^2$ denotes the mean of all the values of V^2 for the various molecules, with corresponding meanings for $\bar{u}$, $\bar{u}'$, $\bar{u}''$, we will have

$$\overline{V}^2 = \bar{u}^2 + \bar{u}'^2 + \bar{u}''^2,$$

and since the molecules do not tend to accumulate in any part of the vessel there will be, on the whole, as many pass across any plane per second in any one direction as in the opposite, or, in other words, the pressure will be equal in all directions, and

$$\bar{u}^2 = \bar{u}'^2 = \bar{u}''^2 = \tfrac{1}{3}\overline{V}^2.$$

Consequently in the general case, when the molecules are moving indiscriminately through the cube with a velocity whose mean square is $\overline{V}^2$, the pressure per unit area will be

$$p = \tfrac{1}{3}mn\overline{V}^2,$$

where n is the number of molecules per unit volume. Now mn is the mass per unit volume, or the density ρ of the gas, consequently[1]

$$p=\tfrac{1}{3}\rho\overline{V}^2.$$

If a given mass M of gas be enclosed in a vessel of volume v, then $M=\rho v$ and the equation becomes

$$pv=\tfrac{1}{3}M\overline{V}^2.$$

Hence if the mean square of the velocities of the molecules remains constant the product of the pressure and volume will be constant. For unit mass we have therefore for all gases the equation

$$pv=\tfrac{1}{3}\overline{V}^2.$$

It is thus proved that the pressure of a gas may be thoroughly explained by the motion of its molecules, and that the supposition of repulsive forces between the molecules is quite unnecessary, as well as being unscientific, molecules being already endowed with the property of mutual attraction. There is one point, however, which should be noticed. By Boyle's law we know that the product pv is constant at constant temperature, and, therefore, the right-hand member of the above equation must be a function of the temperature. The temperature, then, must be measured in some way by $\overline{V}^2$, the mean square of the velocities of the molecules, or by their mean kinetic energy. Hence the heat of a gas must be in some way related to the kinetic energy of its molecules, and the same conclusion may be legitimately extended to all other bodies.

Cor. If several gases be mixed in the same vessel, and if their molecular masses are m_1, m_2, m_3, etc., while the number per unit volume of each is n_1, n_2, n_3, etc., then as before, if their mean velocities are $\overline{V}_1$, $\overline{V}_2$, $\overline{V}_3$, etc.,

$$p=\tfrac{1}{3}m_1n_1\overline{V}_1^2+\tfrac{1}{3}m_2n_2\overline{V}_2^2+\tfrac{1}{3}m_3n_3\overline{V}_3^2+\text{etc.},$$

or

$$p=p_1+p_2+p_3+\text{etc.}$$

That is, the pressure of the mixture is equal to the sum of the pressures which the gases would exert if they occupied the whole space separately. This result was discovered experimentally by Dalton,

[1] This equation enables us to calculate the velocity $\overline{V}$ for any gas, as was shown by Joule. Thus at atmospheric pressure $p=1033$ grammes per square centimetre, and at 0° C. the density of hydrogen is 0·00008957 (gr. per c.c.), hence taking $g=981$, we have for hydrogen at 0° C.

$$\overline{V}=1842 \text{ metres per second.}$$

and is true of course only so long as the molecules do not sensibly obstruct each other.

56. Influence of the Size and Collisions of the Molecules.—In the preceding article we have established the formula

$$pv=\tfrac{1}{3}\overline{V}^2$$

where p and v are the pressure and volume of unit mass, and $\overline{V}^2$ the mean square of the molecular velocities. In deducing this equation the mutual collisions of the molecules have been neglected, and it has also been assumed that when any molecule impinges on the walls of the enclosure the velocity of rebound is equal to that of approach. Hence if these conditions be violated the equation will become modified, and deviations from Boyle's law are to be expected. We shall, therefore, briefly consider the nature of the modifications introduced when the size of the molecules is taken into account, and when the encounters between them become frequent. Let us suppose that the molecules are of radius r, and that t is the time spent in a single collision. It is not to be inferred, however, that in making this supposition we necessarily assume that the molecules are actually spheres of equal and invariable radius. The supposition is made here merely for the sake of simplicity in a first calculation; and, as will appear from the vortex atom theory (Art. 60), the diameter of any molecule may vary from time to time, and the shape may be very different from the simple spherical form.

As a first approximation then, we take the case of a system of equal spheres of radius r. When two equal spheres collide directly they merely interchange velocities, so that if we consider one of them moving with a velocity u to impinge on another, the second takes up the velocity of the first and proceeds with a velocity u, the whole operation being as if the first had passed through the second and proceeded on its journey with unaltered velocity. It would, therefore, appear at first sight as if the motion were unaffected by collision; but there are two items which still require to be taken into account. In the first place, the second ball starts to move at a time t after the first one strikes it, and when it does start it begins to move from a position $2r$ in advance of the impinging ball. There is thus a gain of position $2r$ and a loss of time t, so that if ut is greater than $2r$ the collision will act as a retardation and diminish the number of impacts per second on the walls of the enclosure, but if ut is less than $2r$ the opposite effect will be produced, whereas if ut is equal to $2r$ the collisions will be without effect.

The gain of path, positive or negative, during each collision will

consequently be $2r - ut$, and if l be the mean length of the free path between consecutive collisions, the number of encounters per second will be u/l, and the whole gain of path per second by collision will be

$$(2r - ut)\frac{u}{l}.$$

This is on the supposition that the impacts are all direct. When they are oblique, the gain of path will be some fraction of this quantity,[1] which may be represented by the expression

$$(2r - ut)\frac{u}{l}f,$$

so that the space described per second is changed from u to

$$u\left\{1 + (2r - ut)\frac{f}{l}\right\}.$$

Now the mean free path depends only on the radius of the molecule and the space v through which unit mass is diffused, so that if the former be supposed constant l will vary with v only. It may be shown[2] that l is directly proportional to v, and hence the above expression may be written in the form

$$u\left(1 + \frac{c}{v}\right),$$

where c is a constant depending on the nature of the gas, if ut be supposed to depend only on the nature of the gas.

In the preceding article the pressure on the walls of the enclosure was obtained as the product of two factors—one mu the momentum of a single molecule, and the other the number of impacts per second. The latter will now be proportional to $u(1 + c/v)$, so that the formula $p = \frac{1}{3}\rho\overline{V}^2$ becomes

$$p = \tfrac{1}{3}\rho\overline{V}^2\left(1 + \frac{c}{v}\right),$$

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[1] See Memoir by P. A. Leray, *Ann. de Chimie et de Physique*, 6e, tom. xxv. p. 89, 1892.

[2] Thus if we consider the case of a given mass of gas occupying a certain space, say a cube of side a, then the mean distance between pairs of molecules will be proportional to the linear dimensions of the space, that is, to the side of the cube. For if the distance between each pair of molecules be doubled, the side of the cube will be doubled, and so on. Further, since the molecules are supposed to remain unaltered in size, it follows that when the distance between any pair is altered, the solid angle which each subtends at the other will vary inversely as the square of the distance between them, and consequently the chance of collision will be inversely as the square of the average distance, or the mean free path will be directly as the square of this distance, that is, as the square of the linear dimensions. Hence, on the whole, the mean free path will vary directly as the cube of the linear dimensions of the mass; or, in other words, as the volume.

or for unit mass of the gas

$$pv=\tfrac{1}{3}\overline{V}^2\left(1+\frac{c}{v}\right),$$

where c, as we have already noticed, may be either positive or negative according as $2r$ is greater or less than ut. If the molecules be not spheres, and be unequal, r may be regarded as the mean radius.

57. Molecular Kinetic Energies.—In the foregoing we have only considered the velocity of translation of the molecules. Besides possessing velocity of translation each molecule may be in a state of vibration or rotation, and will possess kinetic energy in virtue of these motions as well. Problems of much greater complexity are, therefore, presented when we consider the effect of these additional motions on the mutual encounters and impacts against the walls of the enclosure. The further question is also presented as to how the total kinetic energy of a molecule is divided between the three components—translation, vibration, and rotation. In a perfect gas it is assumed that it is divided in a constant ratio between the three, so that denoting them by

$$\Sigma\tfrac{1}{2}m\bar{u}^2,\ \Sigma\tfrac{1}{2}m\bar{w}^2,\ \Sigma\tfrac{1}{2}m\bar{\omega}^2,$$

respectively we have

$$\bar{u}^2=a\bar{w}^2, \text{ and } \bar{\omega}^2=b\bar{w}^2,$$

where a and b are constants depending on the nature of the gas.

Hence the equation

$$pv=\tfrac{1}{3}\overline{V}^2$$

may be written in the form

$$pv=\tfrac{1}{3}a\bar{w}^2,$$

and if we define the temperature of the gas as the average kinetic energy of vibration of a molecule, we have

$$\Theta=\tfrac{1}{2}m\bar{w}^2,$$

therefore the equation becomes

$$pv=\tfrac{2}{3}\frac{a}{m}\Theta,$$

or since the whole mass under consideration is unity, and therefore $1/m=n$, the number of molecules, we have

$$pv=\tfrac{2}{3}na\Theta,$$

so that pv is constant if n and Θ are constant. The product pv may therefore vary from either of two causes. Either the average energy of the molecule may vary, or the molecules may form into clusters, so that the number n changes, and when groups of molecules are formed

consequent modifications will be introduced. In the same way the more general equation becomes

$$pv = \tfrac{2}{3} na\Theta\left(1 + \frac{c}{v}\right),$$

or

$$\frac{pv^2}{v+c} = \tfrac{2}{3} na\Theta.$$

58. **Structure of Atoms—Rankine's Hypothesis.**—The hard atom of the Grecian philosophers, although at present in disrepute and out of touch with the more modern scientific conceptions, still survives in a certain sense unrefuted. Rival theories have been developed which are perhaps just as improbable, and perhaps not less illusory. The most inconceivable of these is that of Boscovich, who by mathematical refinement got rid of the material atom altogether, and replaced it by a mere point, or centre of force towards, or from, which certain forces were directed. This view was supported on the assertion that matter can only be known by its effects, and if these can be explained otherwise the assumption of a substance is not necessary. The phenomena of nature were thus to be explained by a mathematical fiction similar to that which in the hands of Gauss and Poisson formed the foundation of the theory of statical electricity.

The first step towards a rational theory was made by Rankine,[1] who about 1842 endeavoured to derive the laws of pressure and expansion of gases from what he termed the *hypothesis of molecular vortices.*

This hypothesis assumes "that each atom of matter consists of a nucleus or central point enveloped by an elastic atmosphere, which is retained in its position by attractive forces, and that the elasticity due to heat arises from the centrifugal force of those atmospheres, revolving or oscillating about their nuclei or central points." No definite supposition is made as to whether the elastic atmospheres are continuous or consist of discrete particles—that is, whether the elasticity of these atmospheres is a primary quality or entirely due to the "repulsion" of discrete molecules. Further, the nucleus at the centre of each molecule may or may not be distinct in nature from the elastic envelope. It may be a portion of the atmosphere in a condensed state, or merely a centre of condensation of the atmosphere. The word nucleus signifies merely the atomic centre, and its volume, if any, is assumed to be inappreciably small compared with that of the envelope. The supposition peculiar to the inquiry is "that the vibration which, according to the wave theory, constitutes radiant heat and light, is a motion of the atomic nuclei or centres, and is propagated by means of their mutual attractions and repulsions." The absorption and emission of heat and light consist in a transference of motion from the nuclei to their atmospheres, and *vice versâ,* and this hypothesis Rankine considered as possessing immense advantages in explaining the propagation of transverse vibrations, the immense velocity of light, and its dispersion as well as its mode of propagation through crystalline media. According to this theory, in the case of perfect fluidity

[1] *Trans. Roy. Soc.*, Edinburgh, 4th Feb. 1850 ; *Phil. Mag.*, Dec. 1851 ; *Scientific papers*, p. 16.

each atomic atmosphere possesses uniform density throughout each spherical layer described round the central nucleus. In other words, the density at any point of the atmosphere is considered as a function of the distance from the centre of the atom. The quantity of heat in a body is measured by the kinetic energy of its molecular revolutions or oscillations. These molecular motions might either be an oscillation of the spherical layers of the atomic atmospheres to and from their centres, or else a vortex motion of the elements of the atmospheres round the radii of the spherical atoms, so that each spherical layer is filled with radial vortices.

Such is Rankine's attempt to explain dynamically the increase of pressure of gases caused by heat, and although it is merely a first trial, and probably is far from the truth, yet in its very name it contains the germs of suggestion which render it not unworthy of its author.[1]

59. Preliminary Considerations on the Possibility of Matter being due to Motion in a Medium.—The question which now presents itself is, What is an atom of matter? By assuming the existence of atoms and molecules, and endowing them with certain qualities, many of the properties of bodies may be plausibly explained, but, granting the existence of atoms, the problem which still remains, and which probably ever will remain, for speculation is, What is an atom? The existence of a fundamental medium, the ether, has already been postulated for many reasons. Being furnished with this medium and motion in it, the problem before us, broadly stated, is "construct the physical universe."

In attacking a problem of this nature we may with profit consider the case of a person furnished with ordinary faculties, and placed in a uniform medium. For the sake of clearness let us take a being capable of moving through a homogeneous ocean, and having no knowledge of its boundaries, or of what is called the top and bottom. The ocean being supposed perfectly uniform in all directions, the supposed person can detect no differences in its properties as he moves through it, and he will consequently be ignorant of his own motion, as well as of the existence of the medium in which he moves. Let us now suppose that at a certain place in the ocean there is a whirlpool, or what is termed a rectilinear vortex. When the being approaches this part of the ocean he will experience certain actions, or sensations, arising from the motion of the medium, and on reflection he will consider that there is something at this place, and will give it a name. This whirlpool will be something to him, and all the rest of the ocean will be void. If other whirls exist at other places he will also regard them as objects,

Being in an infinite ocean.

[1] A germ of Rankine's theory seems to be contained in the older opinion regarding the heat fluid. According to Becher and Stahl the *terra inflammabilis*, or phlogiston, was affected with a rapid whirling motion, *motus vorticillaris*, and when the particles of any body were agitated with this motion it exhibited the phenomenon of heat, or ignition or inflammability, according to the violence of the motion.

and he will be able to determine their positions with respect to each other, as well as his own position and motion with respect to them, so that he is now furnished with the ideas of distance, relative position, and motion. For the sake of distinctness we may assume that by some means he is able to see these whirlpools. For example, they may be in a state of vibration, and may propagate waves in the medium, and these waves may excite a sense appertaining to the being, which for the present we will call the sense of sight. Thus, even though at a distance, he can now detect the whirls by their effect on his senses. The same waves may also affect other senses, for example the sense of heat, or they may not affect either sense, for they may be too long or too short, just as sound waves may be too long or too short to affect the sense of hearing.

Thus a person situated in a homogeneous medium might not be aware of the existence of the medium, but he might be aware of certain parts of it which are in a certain state of motion, and on account of this motion these parts might appear luminous and hot, and possess many other properties which would be discovered through the other senses of the person, and on account of which he would say that these parts were objects, or bodies, or matter, while he fails to recognise the parts of the medium which do not possess this kind of motion. Thus to him certain parts of space would appear occupied by bodies and the remainder would seem to be empty, although all space might in reality be filled with a medium, one part of which differed from another only in the nature of its motion.

The motion of one part or whirl will also be influenced by that of the others, and as a consequence each will exert certain forces on the others, causing them to move towards it or farther away. That is, these whirls might attract or repel each other according to some law determined by the nature of the whirl. By the very motion, then, which constitutes these objects, they would be endowed with a property analogous to gravitation.

Attraction and repulsion.

In connection with this part of the subject it may be well to consider the terms attraction and repulsion which are so freely used in natural philosophy. If two objects which are free move towards each other they are ordinarily said to attract each other, but if they move away from each other they are said to repel each other. When we say the earth attracts a stone, we only mean that a stone will move towards the earth when let go at any point above its surface. When we say that the earth attracts the stone, we do not explain the motion or its ultimate causes, we merely describe it. The introduction of a new word is very satisfying to a certain class of mind,

and often stops further inquiry. There are many who are quite satisfied that a phenomenon is explained when it has received a name.

To exemplify this, let us consider the case of a person situated in an ocean of water on the earth's surface, and ignorant of the top and bottom, and let this person be furnished with a number of pieces of cork and also a number of pieces of stone. Then if he at first takes a piece of cork and a piece of stone simultaneously in his hand and lets them go, he observes that the cork flies in one direction and the stone in the opposite. His first inference is probably that the cork and stone repel each other. He now takes a piece of cork by itself, and he finds that it moves in the same direction as the other piece of cork, and similarly any piece of stone will descend after the other without a piece of cork being near it. He now will probably begin to doubt the truth of his first surmise, that cork and stone repel each other. For he has found that the cork rises just as rapidly whether the stone be near it or not. The force on a piece of either material is the same at all distances from the other, so that the law of force on each of them is independent of the distance or magnitude of the other body. He will probably look beyond his immediate surroundings and begin to speculate in the wildest manner, till by chance he becomes acquainted with the bottom of the ocean. He will now assert that the bottom is the *vera causa* of the motion, and that it repels cork and attracts stone. If, however, he had first become acquainted with the top he would have been quite satisfied that the top attracted the cork and repelled the stone, and when he knows both top and bottom he is furnished with a variety of alternatives. He may say that the top attracts the cork and the bottom attracts the stone, or that the top repels the stone and the bottom repels the cork. Probably the last thing which will strike him will be that the top and bottom may be without influence on both pieces of matter, and that these bodies may also be without direct action on each other, but that their motion in all cases arises from the immediate action of a medium in which they are immersed.

60. The Vortex Atom.—The idea that motion is in some way the basis of what we call matter is an old one, but no distinct conceptions on the subject could be formed till Helmholtz[1] (1858) developed his investigations in fluid motion. In this celebrated paper it was shown that the rotating parts of a perfect, incompressible fluid, in which there is no slipping, maintain their identity for ever, and are thus eternally differentiated from the non-rotating parts. Also that these

[1] Helmholtz, Crelle, 1858; *Phil. Mag.*, 1867.

rotating parts are arranged either in endless filaments forming closed curves, or are terminated only at the boundaries of the fluid; and these vortex filaments, as they are called, may be knotted or linked together in a variety of ways. Thus if we treat the ether as a perfect fluid, then any portion of it in vortex motion must for ever remain so. Such motion can never be created or destroyed, and a portion of the ether possessing it must for ever remain differentiated from the rest. A vortex filament in the ether will thus at once possess the character of permanence demanded for matter. It will be an atom in the true sense, for it can never be severed. The ends of such a filament cannot exist except at the boundaries of the ether, which is supposed to fill all space.

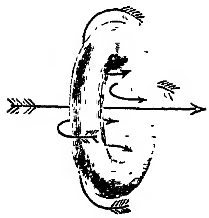


Fig. 2.—Vortex ring.

The vortex atom theory of matter was originated by Sir William Thomson,[1] soon after the appearance of Helmholtz's paper—in fact while witnessing Professor P. G. Tait's beautiful experiments on vortex rings.[2]

Vortex rings are formed when air is puffed through a circular aperture in the side of a box. The smoke rings which some smokers are expert in making are also fairly good examples.

Professor Tait conducted his experiments with the simple apparatus represented in Fig. 3. It consists of a plain wooden box with a

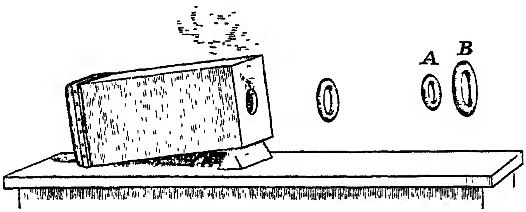


Fig. 3.—Vortex rings in pursuit.

circular aperture, 6 or 8 inches in diameter, in one end. The opposite end of the box is removed and replaced by a tightly stretched cloth or sheet of india-rubber. In order to render the rings visible the air in the box must be impregnated with smoke or fine particles of some floating matter which are distinctly visible. For this purpose the bottom of the box is first sprinkled with a strong solution of ammonia, so that the interior becomes filled with ammonia gas. Hydrochloric acid gas is then generated in the box by simply pouring some sul-

[1] Sir William Thomson, *Proc. Roy. Soc.*, Edinburgh, 1867.

[2] *Recent Advances in Physical Science*, p. 290.

phuric acid into a saucer containing common salt. The hydrochloric acid gas unites with the ammonia and forms a dense cloud of small crystals of sal-ammoniac in the air within the box. If now a sudden blow is applied to the membrane covering the end of the box, a vortex ring issues from the aperture in the other end and moves forward through the room like a solid projectile. When two such rings collide they rebound and vibrate, in consequence of the shock, like bands of solid india-rubber. Vortex rings may, however, be caused to vibrate without impinging on one another. When the hole is circular the rings are circular, and this is the stable form. If the rings deviate from the circular form they will vibrate about that form as a position of equilibrium. Hence to obtain vibrating rings it is only necessary to make the aperture through which they are discharged elliptical, or oval, or even square.

Another curious result deduced by Helmholtz in his paper may also be shown experimentally. If two vortex rings be moving in the same direction with their planes perpendicular to the line joining their centres, the pursuer contracts and accelerates its speed, as A and B, Fig. 3, while the pursued expands in diameter and diminishes in speed, so that the hinder one ultimately overtakes, passes through the other, and takes the lead (shown at A′B′). The same process occurs again, and a system of alternate threading is kept up. If, however, they approach each other from opposite directions, both decrease in velocity and expand indefinitely in diameter, but never reach each other. One behaves to the other as its image in a plane mirror, and the same thing happens when a vortex ring moves up directly towards a plane wall.

As any ring sails through the room it is not only the particles of sal-ammoniac or smoke (which merely render it visible) that remain permanently in it. The air forming its core remains the same, and is the very ring of air which left the aperture of the box. In fact, if there were no fluid friction the ring would not only remain permanently constituted of the same particles of air, but would go on rotating for ever. Once created, it would remain eternal. Vortex rings in a perfect non-viscous fluid thus possess the essential property of indestructibility demanded for matter by chemistry, and in such a fluid it would be equally impossible to create such rings. Theoretically a vortex filament may have a variety of different shapes, and may be knotted or looped about in any manner. In practice, however, it seems possible only to form rings of the simple circular type. An aperture has not yet been devised which will allow the smoke rings to escape in a knotted or looped form.

The motion of the air in the ring is a rotation round the core or central line. If the ring be looked at when approaching the observer from the box, then the particles of air on the inner edge are moving forward, and those on the outside edge are moving backward, from the observer, as shown in Fig 2.

Claims of the vortex atom.

The vortex atom has at first sight very strong recommendations in its favour. It possesses at once many of the essential qualities of matter. It is indestructible and indivisible while its strength and volume remain constant, although its diameter may vary, and if two rings be linked or knotted they must remain so for ever. Again, a vortex ring, when free from the influence of others, moves rapidly forward in a right line, and thus possesses kinetic energy, while it may also vibrate about a form of equilibrium, and in this way give rise to such wave motions in the ether as are supposed to constitute light and radiant heat. The theory is consequently much more fundamental in character than any other, since it merely makes use of a postulated medium, the ether, and the principles of hydrodynamics to explain the properties of matter, and consequently all the phenomena of nature. It does not posit hard atoms endowed with powers of attraction and repulsion, but it endeavours to follow the mechanism by which one molecule influences another, and thus gives a mental representation of the actual processes in action.

The development of the subject is seriously impeded by very formidable mathematical difficulties, and the theory is as yet in its infancy. Only some of the simpler problems have been worked out,[1] and we cannot tell as yet whether the theory will survive the tests which lie before it, when the complete mathematical investigations shall have been worked out, and the results compared with experiment. In making such a comparison, however, it must be kept in view that the experimental work will deal with vortex rings formed in a material fluid, such as air, which is not even approximately perfect in the sense required by the mathematical investigation. The adaptability of the theory will therefore depend on the assumed properties of the ether, and modifications found necessary by future investigation need not overthrow the theory, but rather lead to a knowledge of the necessary properties of the medium.[2]

[1] J. J. Thomson on Vortex Rings: Macmillan and Co., 1883.

[2] Cf. Tait, *Properties of Matter*, p. 21.

SECTION VII

ON ENERGY

61. Motion the Primary Basis of all Phenomena.—If we admit the belief which lies at the foundations of chemical science, namely, that all material substances are built up of simpler substances or elements, which may combine in various manners, but which are unchangeable, and ever retain their distinctive properties, we are led to regard all changes in the universe as ultimately due to changes in the local distribution, or state of aggregation, of elementary matter, and therefore eventually brought about through motion. If, therefore, motion be the primary change which lies at the basis of all other changes, the final aim of physical science must be to determine those movements which give rise to all other phenomena, and trace their origin and progress. The problem thus merges itself into one of dynamics, and all the various so-called forces of nature must be estimated by the same standard, namely, mechanical force, and this, in fact, is expressed in the law of the conservation of energy.

62. All Motion and Energy Relative.—In speaking of motion it must always be borne in mind that all estimation of it is necessarily relative, and for this reason no body considered by itself can be said to be either at rest or in motion. When we say a body is at rest, or moves uniformly in a right line, the estimation is made relatively to some system which we arbitrarily choose as fixed. Force, then, which is measured by the rate of change of motion (the word here meaning momentum, or mass multiplied by velocity) is also relative, and kinetic energy which is measured by half the product of the mass and the square of the velocity is also relative to the same system. Energy, then, in its estimation is relative, simply because velocity is relative.

When we speak of the kinetic energy of a body or system, we always mean the energy with respect to some other chosen system, or else we mean nothing at all. This relativity of energy is sometimes lost

sight of, and it is not uncommon to find the kinetic energy of a body spoken of as something quite independent of all modes of calculation —in fact as an objective reality, a thing existing outside our senses, as the mass of a body is commonly regarded to be.

Energy is again often stated to be only associated with matter, so that matter has been defined as the vehicle of energy; this, however, does not hold according to our limitation of the word matter, for we know that energy in immense quantities is perpetually passing through space with the velocity of light in the form of radiant heat and light, and that it exists also in the so-called potential state. The former exists in the ether, and probably also the latter.

The ether, then, is the great vehicle of energy; and, indeed, it is chiefly on this account that the ether has been postulated. For the sake of distinctness we have agreed not to regard the ether as matter, or a material substance, or as necessarily possessing the distinctive properties of matter, but choose rather to take it as a fundamental medium, and to endeavour to explain all phenomena, matter included, by means of it. If the law of conservation be true, however, the energy in an isolated system is objective like the matter of the system in so far as it is measured relative to a being in the system. To this being the quantity of energy will be definite and constant. It cannot increase or diminish, except by communication from or to the regions outside. To a being outside the system, the energy of the system will depend altogether on the standard of reference, and the question then arises if the matter of the system also varies to that being in a similar manner.

It will consequently be of prime importance to examine the meaning and foundation of the law of conservation of energy, on which all modern physical science has been built.

63. Measure of Energy and the Law of Conservation.—We approach the subject of energy through our ideas of work, or sense of effort. When a weight is raised from the surface of the earth, work is said to have been performed or energy spent. The work done is proportional to the weight and to the height through which it is raised conjointly, and the *measure* of the amount of work done or energy spent is accordingly taken equal to the product of the weight w and height h, or wh. Now if any mass falls under the action of gravity through a height h, the square of its terminal velocity will be $v^2 = 2gh$, so that $\frac{1}{2}mv^2 = wh$, where m is the mass of the body and w is equal to mg. In the same way [1] if the mass m be pro-

[1] It should be carefully noticed that the equation $wh = \frac{1}{2}mv^2$ is not a new relation containing a new physical law, but arises entirely from our definitions of work and

jected vertically upwards with a velocity v, it will rise to a height h given by the foregoing equation, so that the initial velocity v possessed by the mass m will perform the work necessary to raise it to a height h. For this reason we say that a body in virtue of its velocity can do work, and the measure of this work is $\frac{1}{2}mv^2$. We consequently say it possesses energy of motion or kinetic energy.

Conversely the body in descending through a height h could draw an equal mass up to an equal height, or any other weight w' to a height h' given by the equation $wh = w'h'$, so that a body in virtue of its position can do work, and this we call energy of position or potential energy. As thus measured, the two energies are exactly complementary. In the case of a body falling freely, as the potential energy diminishes the kinetic increases, and their sum remains constant. This is the simplest case of conservation, and is beautifully illustrated in the common pendulum. At the highest point of the swing the velocity is zero, and the kinetic energy vanishes. Here the potential is greatest, but as the pendulum falls the potential diminishes and the kinetic increases. The speed of the falling bob increases as it descends, and at the lowest point it possesses a velocity sufficient to raise it to its original level; here the energy is all kinetic and the potential vanishes. At any other point the energy is partly kinetic and partly potential, but their sum has always the same value. If h be the height above the lowest point at any instant, and v the velocity of the bob, then $wh + \frac{1}{2}mv^2$ is the same at all points of the swing.

The same oscillation from kinetic to potential and back again occurs in the planetary system. When the earth is farthest from the sun, her velocity and consequently her kinetic energy is least, but in this position she possesses a balancing store of potential. As she rounds the farthest point of her orbit and begins to approach the sun, she acquires increase of kinetic at the expense of her potential energy. When nearest the sun her velocity is greatest and her potential energy least. As she rounds this nearest point, and begins to retreat

force, and their mode of measurement. Thus force is measured by the rate of change of momentum, or for a body of given mass m

$$F = \frac{d(mv)}{dt} = m\frac{dv}{dt},$$

and work is defined as force multiplied by distance worked through, that is the space integral of the force. Hence

$$W = \int F ds = \int m\frac{dv}{dt}ds = \int m\frac{ds}{dt}dv = \int mv dv = \tfrac{1}{2}mv^2 + C.$$

The work done, therefore, in changing the velocity of a body from v_0 to v is $\frac{1}{2}mv^2 - \frac{1}{2}mv_0^2$, and this follows from the mode of measuring force and work.

from the sun, her kinetic energy begins to diminish; it is used up in doing the work necessary to withdraw the earth against the powerful attraction of the sun, but an equivalent is always stored up ready for use, full tale, without loss, but still without gain. Such is the ebb and flow throughout all nature of the visible energy of the universe. At one place increasing and exhibiting itself, like new life in the motion of her matter; at another diminishing, disappearing, becoming latent, or, as we say, potential, leaving the matter, at least as visible motion, oscillating throughout all the regions of space from potential to kinetic, and from kinetic to potential, but without increase or diminution of the total stock.

Other examples of stored-up or potential energy occur in a wound-up clock, a bent cross-bow or spring, etc. The work done in winding up a clock or watch is stored up as this so-called potential energy, and, being paid out gradually to the machinery, keeps it in motion. The energy spent in drawing a bow reappears again in the kinetic energy of the shaft which flies from it, and perhaps it is in some very similar manner that the vast stores of potential energy are pent up in explosives.

Illustrations of the principle.

Illustrations of the principle of conservation occur in all the ordinary working engines and mechanical contrivances to facilitate labour. A great weight may be raised to a house-top by a single man through the means of a system of pulleys, or a large mass may be moved by a lever; but in all such cases the work done by the man is undiminished by the use of the engine. It merely enables one man to do a piece of work which it might have required ten to do without the engine, but the work done by the one man, measured in the ordinary way, is always equal in quantity to that done by the ten without the engine. This general principle is usually stated for machines in the form, "What is gained in power is lost in speed."

When a body falls freely under gravity it gains velocity or kinetic energy. During its descent, however, the body may be used to perform work, to raise other bodies, or to put them in motion—for example, to turn machinery. This takes place in water-wheels in which the fall of water from a higher to a lower level is utilised to supply the motive-power of mills. In the case of overshot wheels the water escapes over the top of the wheel, and by its descent keeps the wheel in rotation; in the case of undershot wheels the water escapes below the wheel, and turns the wheel by impact. The machinery, in the latter case, is turned not directly by the fall of the water, but by means of the previously acquired motion of the water. The kinetic energy of the water is directly transferred into kinetic energy of the machinery, and

this may be converted into any kind of work. The machinery, for example, may be employed to work a dynamo, and the electric current so generated may drive an electric motor, which may be used to raise weights (or perform any other kind of work), and throughout all these various transformations, if we could arrange that no loss would occur, the output of the motor would be equal to the supply advanced to the water-wheel. The motor would be able to lift all the water back to the level from which it fell. Another variation might be employed, which would embrace other forms of transformation; the electric current might be used to generate heat in a wire, or decompose water, the products of which would unite again in combustion. It would thus supply the furnace of a heat engine, and this engine might be used under certain conditions to raise the water back to its original level, or its power might be distributed in any way to drive dynamos and light our streets and houses.[1]

The windmill is, like the undershot wheel, driven by impact. It derives its motion from the motion of the air; but in both cases the velocity of the water and the velocity of the air are diminished. The energy of motion of the driving material (water and air in these cases) is diminished by an amount equal to that gained by the engine.

The output of such an engine is, however, in practice always less than the supply. Thus a pendulum once started to swing should go on swinging for ever, but in practice this is not the case. The amplitude of the swing gradually decreases, and finally the pendulum comes to rest. It gradually loses its energy. The kinetic energy it possesses at the lowest point of its swing does not raise it to quite so high a level as that from which it fell. One cause of this will be found in the air in which the pendulum moves. During its oscillation the pendulum is continually beating the air away in front. It is setting the air around in motion, and consequently losing a part of its own motion, so that the kinetic energy at the lowest point becomes less and less every swing, till it is finally all frittered away. If there were no air around the pendulum, the motion would still gradually subside from another cause. This arises in the friction at the supports. In

[1] In 1891 a dynamo driven by water-power at Lauffen on the Neckar generated an electric current, which was conducted to the Electrical Exhibition at Frankfort, over 100 miles distant. This current was transformed at Lauffen from one of low to one of high electro-motive force, and on arriving at Frankfort it was transformed back again to one of low electro-motive force. Part of it was then used to illuminate 1200 arc-lamps, and the remainder was employed in driving a pump, which raised water from the mains to the top of an artificial hill, where it descended as a waterfall on the Exhibition grounds. Thus the waterfall at Lauffen was reproduced in part at Frankfort, the energy being transmitted over a distance of 108 miles, and reappearing after several transformations in its initial form.

the same way a fly-wheel turning on an axle gradually loses its motion through friction. Heat, we know, is generated by friction, and the heat produced is, by Joule's experiment, equivalent to a certain amount of work. When heat is produced a certain amount of energy must be spent somewhere, so that if friction occurs in any part of a machine there is a loss of energy there. For this reason, then, the fly-wheel comes to rest. Even though heat were not produced, electrification may be produced, and this would use up part of the energy, and the system would come to rest. If, however, neither heat nor electricity be produced, the energy of the system might be spent in processes of which we have no cognisance. It might be gradually radiated into space, so that, although by experiment we would be unable to account for the dissipation of the energy of the system, yet the principle of conservation might be true. In the same way the machinery might receive energy from the vast store in the ether,[1] and of this we might have no cognisance, so that friction might occur and still the machinery go on for ever. We would then have a kind of perpetual motion, but not necessarily a violation of the doctrine of conservation of energy. From this point of view, the principle can neither be proved nor disproved; it must for ever rest on accumulated evidence.

64. Recapitulation.—In recapitulation, then, we see that an elevated mass can do work by sinking to a lower level, and that it loses its capacity for doing such work as it sinks, that is, in proportion as the work is actually performed. The same applies to springs and elastic bodies in a state of compression or extension, as well as to moving masses. Heat may be employed to do work, but in this process an equivalent quantity of heat is destroyed. Electric currents may be used to do work, but to maintain the current an equivalent amount of work must be spent. Chemical compounds may be decomposed by the expenditure of energy, and the energy may be regained by recombination of the elements. Thus the universal characteristic of equivalence and convertibility prevails in all mechanical, electrical, thermal, and chemical forms of energy. When a quantity of any form is spent, an equivalent of some other form, or forms, is produced.

According to the law of conservation, the universe is endowed with a store of energy which, through all the varied changes of natural processes, can neither be increased nor diminished, but which, though passing through ever-varying phases of transformation, is, like the matter of the universe, unchanging in quantity from eternity to eternity. All

[1] Take, for example, the storage of energy by plants and motion of the radiometer. These operations might also be effected by waves which we could not detect otherwise.

changes and phenomena are due simply to variations in its mode of appearance. Here we find one portion of it as the *vis viva* of masses moving as a whole, or as the vibration of their parts, and there we detect another in the ethereal waves which produce light and radiant heat; while, on the other hand, we locate vast quantities of it in the energy of position of large masses, or of their constituent molecules, under the names potential and chemical energies. This probably is engaged in the process by which one body attracts another and one molecule another, while in perhaps some similar way a portion is distributed in the ether around magnets, or engaged in electrical processes. The principle, as it now stands, has come to be by far the most fruitful generalisation of modern physics, and its truth is supported by every experiment and application of physical principles. There is no department of physical science with which it does not deal and furnish the investigator with an engine of attack of the most powerful character.

65. Historical.—The first clear and distinct statement of the law of the conservation of energy in its general form was published in 1842 by Dr. Julius Robert Mayer[1] of Heilbronn. For a small group of phenomena it had been already stated by Galileo and Newton, and afterwards more definitely by D. Bernoulli, and so continued recognised as applicable to the then known mechanical processes. Certain amplifications were from time to time introduced by such men as Rumford, Davy, Carnot, Séguin, and Montgolfier, and it is probable that more than one of these philosophers had a strong feeling of its perfect generality, but feared to state it without sufficient experimental evidence. This evidence did not exist when Mayer first published his general statement,[2] but still remained to be deduced in that department where the applicability of the law appeared most doubtful, viz. the production of heat from work, and of work from heat. While Joule and Colding independently laboured to establish the law, Mayer was led to it by physiological questions, and with the greatest clearness grasped the principle in its widest generality.

[1] Liebig's *Annalen*, May 1842.

[2] Joule says: "Neither in Séguin's writings, nor in Mayer's paper of 1842, were there such proofs of the hypothesis advanced as were sufficient to cause it to be admitted into science without further inquiry. I believe that the experiment attributed to Gay-Lussac was not referred to by Mayer previously to the year 1845. Mayer appears to have hastened to publish his views for the express purpose of securing priority. He did not wait till he had the opportunity of supporting them by facts. My course, on the contrary, was to publish only such theories as I had established by experiments calculated to commend them to the scientific public, being well convinced of Sir J. Herschel's remark that 'hasty generalisation is the bane of science'" (Joule, *Phil. Mag.*, 1864, part ii., p. 151; see also 1862, part ii., p. 121). Joule's experiments were commenced in 1840.

He also pointed out that the dynamical equivalent of heat was a fundamental constant to be determined by experiment, and assuming that the work done in compressing a gas is the equivalent of the heat generated, he deduced the number 367 gr. met. from the values of the two specific heats of air available at the time (see p. 243). With regard to this method, which will be described elsewhere (p. 250), it may be remarked that the substance operated on does not pass through a complete cycle of changes; it is not in the same condition at the end of the operation as at the beginning, and consequently it is not legitimate to assume that the heat evolved is the sole effect of the work spent in compressing the gas. The volume is changed, and it is quite impossible to say *a priori* whether this change may not involve an expenditure of work such as is employed in winding up a spring. Three years previously (1839) Séguin had given expression to the same ideas regarding the equivalence of heat and work, and had obtained the value 369 by a similar method, and it appears from the last edition of Carnot's works that at least before 1832 (the date of his death) this distinguished scientist had not only embraced the dynamical theory of heat, but had planned many of those very experiments by which Joule subsequently established the equivalence of heat and work. He also gave an estimation of this equivalent (370), probably deduced from the same data as those employed by Mayer. It thus appears that the principle of equivalence was harboured by nearly all the great scientific thinkers of the early part of this century, and that the general doctrine of the conservation of energy grew in a more or less gradual manner as experience became more and more extended. Great service was undoubtedly rendered to science by Mayer's distinct and comprehensive statements, but at the time he made these statements, Joule was conducting his experiments on the dynamical equivalent of heat, and Colding was presenting important papers on the same subject to the Royal Scientific Society of Copenhagen. It does not seem just, therefore, to assign to any particular person the credit of establishing the general principle, or to regard any particular man as the father of the doctrine of the conservation of energy, but one thing is certain, namely, that Joule was the first to make an accurate determination of the dynamical equivalent of heat, and that the final development of the methods of applying the doctrine in detail to the problems which occur in the science of heat was mainly due to the simultaneous work of Clausius, Rankine, and William Thomson between 1849 and 1851.

Much about the same time Helmholtz independently set himself to work out the principle from a mathematical point of view, and

showed[1] that the energy of any system must be conserved by starting with Newton's laws of motion, and the supposition that matter consists of particles which act on each other with forces directed along the lines joining them, and which depend only on the distance.

No absolute proof.

The general principle of the conservation of energy is not, however, to be proved by mathematical formulæ. A law of nature must be founded on experiment and observation, and the general agreement of the law with facts leads to a general belief in its probable truth. Further, the conservation of energy cannot be absolutely *proved* even by experiment, for the proof of a law requires a universal experience. On the other hand, the law cannot be said to be untrue, even though it may seem to be contradicted by certain experiments, for in these cases energy may be dissipated in modes of which we are as yet unaware. The universe is regarded as infinite, and the energy stored in it may be legitimately regarded as infinite also, and the proof of the conservation of an infinite quantity does not seem to be a legitimate inquiry.

66. On Potential Energy — all Energy probably Kinetic.—It may not be out of place to examine here the meaning of the term potential energy. When a body is projected vertically upwards its velocity gradually decreases, the kinetic energy which it possessed at the beginning of the flight gradually leaves it as it rises, and when the body reaches its highest point all its initial energy of motion has disappeared. The question then arises, what has become of the energy of motion of the body? We say it has become potential, that it has become latent or has disappeared, or ceased to exist as visible motion, or that it has been used up in raising the body from the earth. This, however, is by no means an explanation of what has happened. It teaches us nothing further as to the process in operation during motion. Observation shows us that the body possesses motion initially, that as it rises the motion is gradually lost, and that it is gradually regained as the body returns to earth. The word potential energy here is only a name for the difference between the initial kinetic energy of the body when starting in its upward flight, and that possessed at any other point of the path. This, we have seen, may be represented by the expression wh, where w is the weight of the body and h the height it has ascended. In the same way the potential energy of an isolated system of masses in any configuration merely denotes the difference between the kinetic energy of the system in that configuration, and the kinetic energy in some other chosen configuration (generally chosen as that of maximum kinetic energy).

[1] Helmholtz, *Erhaltung der Kraft*, 1847.

The question still remains, what becomes of the motion when the kinetic energy of a system diminishes? Can motion ever be changed into anything else than motion? If we assume a fundamental medium whereby to explain all the phenomena of nature, then the properties of this medium ought to remain unchanged, and all other changes must be explained by motion of the medium. Such an assumption is quite philosophic, and the method of procedure is certainly scientific. An evident reply to the question of what becomes of the motion of a projectile rising upwards is that it passes into the ether. The first assumed property of the ether is that it can contain and convey energy. There is no *a priori* reason, then, why the energy of motion of a projectile as it rises upwards should not be stored up as energy of motion of the ether between the body and the earth, or elsewhere. The oscillation from kinetic to potential, and from potential to kinetic, in the case of the pendulum is then, from this point of view, merely an interchange of energy of motion going on between the mass of the pendulum and the ether around it. According to this view all energy is energy of motion, and must be measured by the ordinary mechanical standard. The work we do in lifting a body from the earth is spent in generating motion in the ether, and as the body falls this motion passes from the ether to the body, which thus acquires velocity. In the same way, the work spent in generating electric currents and electrifying conductors must be represented as spent in generating motion of the ether around the electric circuits and conductors. On the vortex atom theory of matter this view is quite intelligible, for here we have nothing but ether and motion in the universe, so that all change must be interchange of motion. If motion passes from one body it must either pass into other bodies or else into the ether, so that all energy is kinetic, and what we call potential energy, or energy of position of a system, is energy of motion in the ether, which has left the system and become located in the ether, and which may be regained by the system from the ether. The oscillation of energy, then, is from ether to matter, and from matter to ether, and on this oscillation all the physical life of the universe depends.

Kinetic energy in the ether.

A rough mental picture of the process might be obtained as follows. We might suppose a body connected to the earth by vortex filaments in the ether, which would replace the lines of force. The ether is spinning round these lines, and when the body is lifted from the earth the work done is expended in increasing the length of the vortex filaments. The work is thus being stored up as energy of motion of the ether, and when the body falls to earth the vortex

lines diminish in length, and their energy of motion passes into the body and is represented by the kinetic energy of the mass.

67. Perpetual Motion—Indestructibility of Matter.—The object of the perpetual-motionists was to construct an engine which would work continually without the aid of any external driving force—an engine which would do work without fuel or any other supply of energy. The solution of this problem promised enormous gains, and bid fair to replace the gold-hunting operations of the alchemists. Work is wealth, and a machine which could work without fuel would prove as profitable a possession as the philosopher's stone. The possibility of perpetual motion in this sense, viz. the creation of energy, is opposed to the law of conservation, which is now universally accepted as the foundation of physical science. Still it would be quite consistent with this law to construct an engine which would go on working without expense to the owner, other than the wear and tear of the machinery. An actual example of such an engine is a water-wheel. Here the driving power costs nothing, except there be a river tax; it comes indirectly from our great reservoir, the sun. In the same way, on a small scale, Crooke's Radiometer is more directly driven by the heat of the sun, and there is no *a priori* reason why the ingenuity of man should not utilise the vast stores of energy which are located in the ether, and ever traversing it, to drive his engines.

So also, if matter be vortex motion in the ether, it is not impossible that the constitution of the ether may be such that the very motion which constitutes matter may in time be used to serve the purposes of man. That matter, in fact, may not be indestructible or uncreatable, but that man may yet discover the means of so directing the motions already existing in the ether, that any one kind of motion may be converted into any other at will, and still the law of conservation may hold throughout. Such speculations are, perhaps, visionary, but still they are not out of place, for they tend to overthrow dogma as to what must or must not happen. If the ether fills the universe, and if it contains energy throughout, then the store is infinite; and with this infinite store at our disposal what may not be possible when we discover the means of using it?

Indicator Diagrams

68. Graphic Representation of the State of a Substance.—An exceedingly fertile and lucid method of treating many physical problems was introduced by Watt, the celebrated improver of the

steam-engine, and is known as the graphic method. This consists in representing the pressure and volume of a substance by the co-ordinates of a point, so that each point in the plane of the figure corresponds to a definite pressure and volume, and therefore represents a definite condition of the substance. The state of the substance may, therefore, be said to be determined or represented by the position of the corresponding point in the diagram. The method was devised by Watt for the purpose of determining the work done by a steam-engine, and it is still employed for that and similar purposes. Subsequently Clapeyron employed it to interpret the work of Carnot, and it has since been adopted and used with great advantage in every branch of science, especially in the domain of thermodynamics, where it often proves itself easily intelligible to those who cannot follow the more complicated analytical investigations.

Let OX and OY (Fig. 4) be two fixed rectangular lines chosen as axes of reference; then the distances OA′ and AA′ of any point A from these lines completely determine the position of A. These distances are termed the co-ordinates of the point, and when they are known the point A can be found.

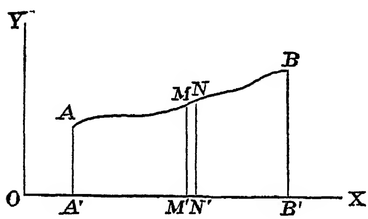


Fig. 4.

Hence, if pressures are measured parallel to OY and volumes parallel to OX, so that AA′ represents the pressure of a substance and OA′ its volume (per unit mass), then the position of A on the figure represents the state of the substance as regards pressure and volume. Every position of A corresponds to a definite condition of the substance, for when the pressure and volume are known the temperature is in general completely determined. Sometimes, however, two or more different temperatures may be possible at the same pressure and volume, as happens in the case of water for an interval above 4° C., between 4° and 0°, and below 0° C. To represent the state of the substance completely then, it is only necessary to erect a perpendicular at A to the plane of the figure, and to measure off along this perpendicular a length representing the temperature (or lengths representing the temperatures) corresponding to A, and as A moves about over the plane the extremity of the perpendicular will describe a surface in space which will represent the characteristics of the substance, every point on the surface corresponding to a definite condition of the substance. Thus, if the characteristic equation connecting the pressure, volume, and temperature be $f(p, v, \theta) = 0$, then this will be the

Characteristic surface.

equation of the foregoing surface, and p, v, θ will be the rectangular co-ordinates of any point on it.

Returning, however, to the case of two rectangular axes: if we suppose A to move along any curve AB, this will represent that the substance passes from A to B through a perfectly definite series of conditions, the pressure and volume in each condition being represented by the co-ordinates of the corresponding point on the curve AB. In general, the temperature corresponding to any point will vary from point to point, so that in order to effect the transformation indicated by the curve AB heat must be supplied to, or taken from, the body, as it passes from point to point of the curve, in a manner which becomes completely determined when the nature of the curve is known. It may of course happen that the temperature of the substance remains constant throughout the transformation, and in this case the curve AB is termed an *isothermal* line, and a transformation may also be such that heat is neither added to, nor taken from, the substance at any stage of the process, and in this case the transformation is said to be *adiabatic*, and the curve is called an adiabatic line.

69. Graphic Representation of Work.—When a substance passes from the condition A (Fig. 4) to the condition B its volume has increased by an amount A′B′, and, as it has been under pressure (varying according to a definite law) throughout the transformation, it follows that work has been done by the body in expanding against this external pressure. This is termed the external work, and it is easy to show that it is represented by the area ABB′A′, included between the curve AB, the axis OX, and the ordinates AA′ and BB′. For this purpose let us take the case of a substance, say a gas, enclosed within a cylinder which is closed by a piston of area A. Let p be the pressure (per unit area), and let us suppose this remains constant while the piston is pushed forward through a distance x (which we can suppose as small as we like). The whole pressure on the piston is pA and the work done is therefore pAx, but Ax is the change of volume, so that if we denote it by dv, the work done in compressing the substance by an amount dv will be pdv. Referring again to Fig. 4, we see that if the substance passes from M to an adjacent point N, the volume changes by an amount $M'N' = dv$, and that the external work pdv is consequently represented by the narrow strip of area MNN′M′. Hence the whole work done in passing from A to B is represented by the area ABB′A′—that is,

$$W = \text{area } ABB'A' = \int p\,dv.$$

If the equation of the curve be given, p can be expressed as a

function of v, and the integral expressing the area ABB′A′ may be evaluated.

The external work done while a substance passes from any state A to any other state B depends, therefore, not only on the positions of these points, but also on the nature of the curve AB, along which the transformation takes place. Hence, if a substance be caused to pass from A to B along the path AMB (Fig. 5), an amount of work represented by AMBB′A′ will be done by the substance while it expands, and if it be caused to return from B to A along a different path BNA, an amount of work represented by the area BNAA′B′ will be done on it by compression, so that throughout the whole operation, while the substance passes round the complete cycle AMBNA, a quantity of work represented by the area of the cycle is done by the substance. If, on the other hand, the substance had passed round the cycle in the opposite direction ANBMA, the work represented by the area of the cycle would have been done on the substance, for in this case the expansion takes place along ANB at the lower pressures and the compression is effected at the higher.

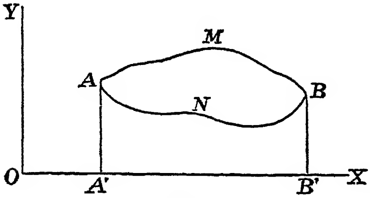


Fig. 5.

Closed cycle.

We have thus the general result that if a substance be made to pass through any complete cycle of operations, returning to its initial condition, so that the indicator diagram is a closed curve, the external work done is represented by the area of the cycle, and is done by, or on, the body according to the direction in which the cycle is described. If the direction of motion opposite to that of the hands of a watch be taken as positive, while the opposite is considered negative, then when a cycle is described in the positive direction a positive quantity of work, represented by the area of the cycle, is done on the substance; but if it be described in the negative direction a negative quantity of work, represented by the same area, will have been done on the substance, negative work done on the substance being merely work done by it.

The first law of thermodynamics informs us now that when a substance passes through any closed cycle of transformations, and returns again to its initial state, the area of the cycle is the mechanical equivalent of the heat evolved or absorbed by the substance during the process. It is very important to notice, however, that when the cycle is not closed, so that the body has not returned to its initial condition

A, but is in some other state B, then the heat supplied to the body is not the equivalent of the external work done, but is used up partly in doing this work and partly in altering the thermal condition of the substance. When the cycle is completed the body has returned to its initial condition, and for this reason the external work is, in this case, the equivalent of the heat supplied during the cycle.

Examples

1. Show that the isothermal lines for a perfect gas are a system of rectangular hyperbolas.

[The equation of any isothermal will be pv=constant, and this is the equation of a rectangular hyperbola having the axes of reference for asymptotes.]

2. In the case of a gas prove that the isothermal elasticity is equal to the pressure.

[The elasticity of a substance is the reciprocal of its compressibility, and the latter is the change of volume, per unit volume, for unit increase of pressure. Hence, if a volume v changes by an amount dv for increase of pressure dp per unit area, the change per unit volume for unit increase of pressure will be $-\frac{1}{v}\frac{dv}{dp}$, so that the elasticity will be

$$-v\frac{dp}{dv}.$$

Now for the isothermal changes of a gas pv=constant, therefore $p+v\frac{dp}{dv}=0$, or $-v\frac{dp}{dv}=p$.]

3. If a tangent drawn to an indicator curve at any point P (Fig. 6) meets the axis of pressure at L, and if M be the foot of the perpendicular from P on the same axis, show that the elasticity of the substance at the point P of the transformation is represented by LM.

[We have LM=MP tan LPM=v tan LPM$=-v\frac{dp}{dv}$, ∴, etc.

Since the intercept made by the asymptotes on any tangent to a hyperbola is bisected at the point of contact, it follows that LM=MO in the case of a gas during an isothermal transformation; or the isothermal elasticity of a gas is equal to the pressure.]

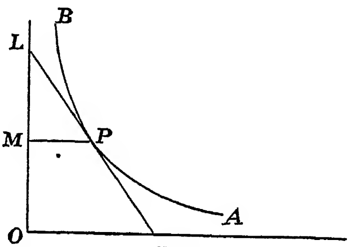


Fig. 6.

4. Prove that the adiabatic lines of a substance, in which compression causes increase of temperature, are steeper than the isothermal lines.

[For a given value of dv the increase of pressure dp will be greater for the adiabatic transformation than for the isothermal, on account of the increase of temperature, and therefore LM will be greater.]

5. Assuming the adiabatic equation of a gas to be

$$pv^{\gamma}=\text{constant},$$

prove that the adiabatic elasticity is γp, and hence that γ is the ratio of the adiabatic to the isothermal elasticity.

70. Mean Kinetic Energy of a System of Material Particles in Stationary Motion.—When the velocity of a point fluctuates between certain limits while the point oscillates about a mean position, the motion is said to be stationary. All periodic motions, such as the vibrations of an elastic solid, are of this kind, and such also is supposed to be the molecular motion of a body which constitutes its heat.

In Art. 55 we considered the behaviour of a system of molecules so thinly scattered that their mutual influence might be neglected; we shall now consider the case in which the molecules are close to each other, and within the sphere of each other's attraction.

Let the co-ordinates of any molecule[1] be x, y, z, and let the component forces on it parallel to these axes be X, Y, Z. Then $m\frac{d^2x}{dt^2}=X$.

But by differentiation we find

$$\frac{d^2}{dt^2}\left(x^2\right)=2\frac{d}{dt}\left(x\frac{dx}{dt}\right)=2\left(\frac{dx}{dt}\right)^2+2x\frac{d^2x}{dt^2}.$$

Hence

$$\tfrac{1}{2}m\left(\frac{dx}{dt}\right)^2=\tfrac{1}{4}m\frac{d^2(x^2)}{dt^2}-\tfrac{1}{2}xX.$$

The mean value of the left-hand member during any time t will be

$$\frac{m}{2t}\int_0^t\left(\frac{dx}{dt}\right)^2dt=\frac{m}{4t}\left[\frac{d(x^2)}{dt}-\left(\frac{d(x^2)}{dt}\right)_0\right]-\frac{1}{2t}\int_0^t xX\,dt.$$

The two terms involving the sign of integration in this equation are the mean values of the quantities under this sign, during the time t. For periodic motions t may be taken the periodic time, and in this case the first term of the right-hand member of the equation will vanish, for $\frac{d(x^2)}{dt}$ will have the same value at the beginning and end of a complete period. We will then have

$$\text{mean value of } \tfrac{1}{2}m\left(\frac{dx}{dt}\right)^2=-\text{mean value of } \tfrac{1}{2}xX.$$

For irregular motions such as those which occur in gases and liquids, we need only suppose t large compared with the time that a molecule moves steadily in the same direction. The term within the square bracket will vary within certain limits; and as it is divided by t, it follows that when t is large this term becomes negligible. The same reasoning applies to the motions parallel to the axes of y and z, so that we have

$$\text{mean of } \tfrac{1}{2}\Sigma m\left[\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right]=-\text{mean of } \tfrac{1}{2}\Sigma(xX+yY+zZ),$$

or

$$\text{mean of } \tfrac{1}{2}\Sigma(mV^2)=-\text{mean of } \tfrac{1}{2}\Sigma(xX+yY+zZ).$$

This mean value has been termed by Clausius the *virial* of the system, and theorem may therefore be stated in the form "the mean kinetic energy of the system is equal to its virial."

Cor. 1. If the force between two particles be $\phi(r)$ a function of the distance r between them, then if x, y, z and x', y', z' be the co-ordinate of the particles, we have for one

$$X=\phi(r)\frac{x-x'}{r},\quad Y=\phi(r)\frac{y-y'}{r},\quad Z=\phi(r)\frac{z-z'}{r},$$

[1] Clausius, *Phil. Mag.*, August 1870.

with equal and opposite values of X, Y, and Z for the other, therefore

$$Xx + X'x' = X(x - x') = \phi(r)\frac{(x - x')^2}{r},$$

with corresponding expressions for the other two co-ordinates, so that

$$\tfrac{1}{2}\Sigma(xX + yY + zZ) = \tfrac{1}{2}\Sigma r\phi(r).$$

COR. 2. In the case of a gas enclosed in a vessel a uniform normal external pressure p exists all over the surface of the mass, and the virial of this will be

$$\tfrac{1}{2}p\int xdydz + \tfrac{1}{2}p\int ydzdx + \tfrac{1}{2}p\int zdxdy = \tfrac{3}{2}pv,$$

where v is the volume of the gas.

Hence in this case we have

$$\tfrac{1}{2}\Sigma mV^2 = \tfrac{3}{2}pv + \tfrac{1}{2}\Sigma r\phi(r),$$

or

$$pv = \tfrac{1}{3}\Sigma mV^2 - \tfrac{1}{3}\Sigma r\phi(r).$$

Consequently if the molecules are out of the sphere of each other's attraction, that is, of $\phi(r) = 0$, the product of the pressure and volume will be equal to two-thirds of the mean kinetic energy of the molecules; but if the molecules are within the sphere of each other's attraction, the effect is to diminish the product pv by an amount equal to two-thirds of the virial of the intermolecular forces. Hence, when a gas is compressed it is anticipated that the product pv will vary and not remain constant at constant temperature. The experimental investigations on this point will be considered later on (see Art. 219).

CHAPTER II

THERMOMETRY

SECTION I

LIQUID THERMOMETERS

71. Discontinuous Thermoscopes.—A thermoscope is an instrument for indicating relative temperatures, and its indications may be either continuous or discontinuous according to the property of matter employed. In continuous thermoscopes a property of matter which varies continuously is made use of, such as change of volume with heat, and the indications of discontinuous thermoscopes depend on the employment of some abrupt change of state, such as fusion. Any substance acts as a thermoscope, solids for a single temperature and liquids for two temperatures. Thus a piece of paraffin wax immersed in a bath will indicate whether the temperature of the bath is above or below the temperature of fusion of the wax, and by this means we could separate a series of given temperatures into two sets, those higher than the melting point of the wax and those lower. In the same way a piece of butter will tell us whether the temperature of a room is higher or lower than the melting point of butter. A liquid gives us more information; it tells us whether a temperature is higher or lower than either the boiling point or the freezing point of the liquid. The water in a basin not only tells us that the temperature of the room is higher than the freezing point of water, but also that it is lower than the temperature of boiling. It thus places the temperature of the room between two others, which are definite and recoverable.

If an instrument merely indicates whether the temperature of a body to which it is applied is higher or lower than a single definite temperature, it is called a single intrinsic thermoscope, because its indication depends upon some intrinsic quality of the instrument. The paraffin wax referred to is a single intrinsic thermoscope, the single temperature being its melting point, and the intrinsic quality the melting of the wax always at this definite temperature.

A multiple discontinuous intrinsic thermoscope shows several

definite temperatures, or indicates whether the temperature of any body to which it is applied lies between any pair of these temperatures. Such an instrument may be constructed by preparing a system of metallic alloys or other substances arranged and numbered in the order of their melting points, and a multiple intrinsic thermoscope has been constructed on this plan in a form convenient for use by Mr. J. J. Coleman.[1] It consists of a set of paraffins which melt at definite temperatures between 40° and 100° F., and mixtures of glycerine [2] and water which freeze at temperatures from 30° to − 35° F. By multiplying the number of substances in such an instrument the system of definite temperatures which it indicates may be made to approach each other closer and closer. Ideally the system may be made nearly continuous by making a system of alloys with fine enough gradation of composition, but the method is essentially discontinuous.

72. Continuous Thermoscopes and Thermometers.—A thermoscope becomes continuous in its indications when the property of matter employed varies continuously with temperature. When such an instrument is properly graduated according to some arranged scale, it not only indicates whether the temperature of a body to which it is applied is higher or lower than some definite temperature, but it also informs us how much it is higher or lower, according to the chosen scale. In this case the instrument becomes not merely an indicator, but also a measurer of temperatures, and is termed a thermometer. In selecting a system of thermometry, any physical property of matter

[1] J. J. Coleman, *Proc. Phil. Soc.*, Glasgow, 1884, vol. xv. p. 94.

[2] Glycerine when pure crystallises a little below 0° C., but when mixed with a little water its freezing point is about 40° C. below zero, and the solidification here is not of a crystalline but of a buttery nature. By varying the quantity of water the freezing point may be varied at pleasure.

A discontinuous intrinsic thermoscope for the measurement of high temperatures was proposed by Prinsep (*Phil. Trans.*, 1828, p. 79). He formed a series of definite percentage alloys of silver and gold, and of platinum and gold. These alloys gave a series of fixed temperatures between the melting points of silver and gold and of gold and platinum. An observation is taken by exposing in a small cupel a set of small flattened specimens of the alloys, not necessarily larger than pin-heads, and noticing which of them are fused. The temperatures of fusion of these alloys have been determined by Erhard and Shertel by a porcelain-air-thermometer (*Jahrb. fur das Berg-und-Hutten-Wesen in Sachen*, 1879). An objection has been raised to Prinsep's alloys on the ground of silver taking up oxygen at high temperatures and ejecting it again on cooling, which renders it inadvisable to use the same specimen twice.

A similar method has been employed by Carnelley and Carleton Williams (*Chem. Soc. Journal*, 1876, 1877, 1878), in which metallic salts with high fusing points were used instead of alloys. The fusing points were initially determined by the calorimetric method.

which varies continuously with heating might be chosen. We have already described how temperature may be defined and measured by the apparent volume of mercury enclosed in a glass vessel (p. 17). If this be taken as our standard instrument, then all other thermometers must be graduated by comparison with it, so that when placed in the same uniformly heated bath they may all agree in their indications. We will thus have a uniform system of measurement, and experiments conducted at any place may be repeated at any other.

The main object to be secured in thermometry is that all thermometers shall be strictly comparable, and since liquid thermometers are easily portable the simplest means of obtaining this object is by comparing all thermometers, directly or indirectly, with some standard instrument. All thermometers would then be copies of the same original, and would agree perfectly in their indications. This being arranged, thermometers may be constructed of other liquids than mercury, or by measuring, not the increase of volume, but the increase in length of a bar, or the increase in pressure of a gas kept at constant volume, or the change in electrical resistance of a wire, or change in pressure of the saturated vapour of a liquid, or change in shape of a spiral composed of strips of different metals, or change in the shape of a single elastic solid subject to stated stress. Standardising.

The condition implied in all cases is that the thermometers shall all be graduated according to the same standard, and that the property of matter made use of shall always give the same indication when the temperature is brought again and again to the same value. It is upon this last property that the accuracy of a thermometer depends. The constitution of the material with which the instrument is constructed must be permanent, so that the property made use of in measuring temperatures is always the same at the same temperature.

The sensibility or delicacy of the instrument depends only upon the recognisability of changes in the indicating property with very small changes of temperature. A thermometer may be delicate in two ways—(1) when it detects very small changes of temperature, and (2) when it rapidly assumes the temperature of any body with which it is placed in contact. The delicacy of a thermometer is consequently to some extent similar to that of a balance, one of the circumstances determining it working in opposition to the other. Thus, in order to secure the first condition the bulb should be large and the bore narrow; but in order to secure the second the bulb should be small, have a large surface, and be filled with a liquid which will rapidly take up the temperature of the medium in which it is immersed, that is, of high conductivity. If the bulb is large the weight of the contained Sensibility.

liquid produces strain effects which may seriously affect the accuracy; and if the initial temperature of the thermometer differs from that of the body with which it is placed in contact, the final indication of the instrument will not be the initial temperature of the body, but will be intermediate between that of the body and the initial temperature of the thermometer. This final reading will differ from the original temperature of the body more and more the greater the heat capacity of the thermometer, the less that of the body, and the greater their initial difference of temperature. In the construction of a thermometer, then, the nature of the work for which it is intended must be taken into account. A thermometer which is best adapted for one class of work may be quite unsuited for another.

73. Construction of a Liquid-in-glass Thermometer.—We shall now briefly describe the construction of a liquid-in-glass thermometer, such as the ordinary mercury thermometer. Such a description, besides being important in itself, affords an excellent example of the method by which the scientific investigation of such a phenomenon as temperature must be proceeded with. In making a thermometer a glass tube possessing a uniform capillary bore is selected, and a bulb of suitable size is blown (or fused) on one end, the other end being left open. It is important that the bore of the tube should be as uniform as possible, and this should be ascertained beforehand by sliding a short thread of mercury through the tube, and observing its length in different parts. If this length is approximately the same at all parts of the tube the bore is fairly uniform, and the tube may be employed. Slight want of uniformity can be corrected for afterwards, as will be explained immediately. The tube and bulb should now be well cleaned, and all organic matter removed from its inside surface by means of boiling nitric acid.

Some of the best thermometer tubes are furnished with a pear-shaped reservoir or funnel at the open end, to facilitate the process of filling. If such a reservoir be not already attached, the end of the tube may be simply bent round, so that it may be dipped with facility under the surface of some mercury or other liquid with which it is desired to fill the instrument.

In order to introduce the liquid, the empty bulb is heated over a lamp, and the air within expands and is partly expelled. The open end of the stem is immediately dipped under the surface of the liquid, and kept there while the bulb and the enclosed air cool. During this process the pressure of the air within diminishes, and some of the liquid is forced through the stem into the bulb by the pressure of the atmosphere outside. By this means the bulb is partially filled. To

complete the process, the liquid thus introduced is boiled till all the air is expelled, and the instrument contains only the liquid and its vapour. If the open end be dipped into a cup of the liquid while the boiling is still in operation, and if the instrument be allowed to cool, the vapour will condense, so that the bulb and stem will become completely filled with the liquid.

The process of filling a thermometer is a matter of some difficulty to a beginner, as it is by no means easy to ensure that all the air has been expelled. Minute bubbles are nearly always found remaining, which adhere with the greatest pertinacity to the sides of the glass and resist expulsion. Caution must also be exercised in the process of boiling the liquid, especially in the case of mercury, which has a high boiling point, and if heated over a lamp the bulb may fuse and lead to disaster. To avoid this a special heating apparatus may be used, by means of which the bulb and stem may be gradually heated throughout its entire length to the boiling point of the liquid.

When the bulb and stem are filled the instrument is raised to the highest temperature that it is intended to measure, and in this state the end of the tube is hermetically sealed. In order to avoid bursting when the thermometer is inadvertently subjected to temperatures higher than the highest that it is intended to register, the upper end of the bore is, in the best instruments, widened out into a small reservoir into which the mercury may expand. This reservoir is important, as it not only prevents the danger of bursting, but can be used to contain some of the mercury separated from the bulb in the process of calibrating, as well as in the separation of minute air bubbles, if any exist in the bulb. Besides, by placing some of the mercury in it the same part of the scale can be used, if desired, at a high and also at a low temperature.

If now the size of the bulb and the length of the stem have been properly adjusted, the bulb and a small part of the stem will be filled with liquid at the lowest temperature which the instrument is intended to register. In this case the fixed points may be determined and the process of graduation proceeded with.

74. Determination of the Fixed Points.—In order to furnish a thermometer with a scale, two points are first marked on the stem which correspond to two definite temperatures. The temperatures generally chosen for this purpose are those originally suggested by Hooke,[1] and adopted by Newton, namely, the melting point of ice and the boiling point of water. The temperature of boiling water is not now employed, but rather the temperature of the vapour of water

[1] Hooke, 1681; see Birch's *History of the Royal Society*, vol. iv.

boiling under the pressure of one standard atmosphere. This pressure is that exerted at the freezing point by a column of mercury 760 mm. high in the latitude of Paris, which is equivalent to a column of 29·905 inches in the latitude of London. The temperature of the steam is chosen, because it is found that the temperature of boiling water depends to some extent on the presence of impurities and the nature of the vessel in which it is boiled, whereas the temperature of the steam depends only on the pressure, the former point having been established by Gay-Lussac and the latter by Rudberg.

The Freezing Point.—The freezing point, as the lower fixed point is called, is determined by placing the thermometer in a vessel containing broken ice, from which water is dripping, so that the bulb and stem, as far as it is filled with mercury, are surrounded with ice, and the top of the mercurial column is just visible. The vessel (Fig. 7) is usually shown with a perforated bottom, so that as the ice melts the water drips away, and the thermometer is surrounded with ice at the melting point. After standing for some time the level of the mercury becomes stationary, and a mark is carefully traced on the glass at this point.

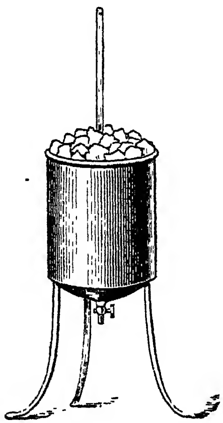


Fig 7.

The advantage gained by allowing the water to drain away as the ice melts is not obvious. As long as there is plenty of ice present the temperature of the water will remain stationary, and the pressure on the bulb of the thermometer will be more uniform than when the water is allowed to drain off. In the latter case angular fragments of ice will be sometimes pressed with their sharp edges against the bulb, and this may cause distortion and consequent displacements of the zero point.

Another question which presents itself is—does the temperature of melting ice depend on whether the ice has been formed from ordinary or distilled water. Both these points have been examined by Mr. F. D. Brown,[1] and his conclusions, after a series of observations on different kinds of ice, and mixtures of ice and water, were that a constant temperature is more rapidly and certainly obtained with a mixture of ice and water than with ice alone. That the temperature thus obtained is really that of melting[2] ice, and that it is preferable to wash and mix the ice with distilled water, as ordinary water lowered

[1] F. D. Brown, *Phil. Mag.* vol. xiv. 1882.

[2] This, however, will depend on what is meant by the *temperature of melting ice*.

the temperature to a slight extent. The quantity of water mixed with the ice should be just sufficient to fill up the spaces between the fragments.

Boiling Point.—The boiling point is determined, as already stated, by placing the thermometer in the steam[1] of boiling water, the pressure being one standard atmosphere. The thermometer is so far plunged into the steam that the surface of the mercury is just visible, as shown in Fig. 8. When the level of the mercury becomes stationary, a mark is made on the stem at its surface, and this is the boiling point. The pressure corresponding to a standard atmosphere is in this country taken to be that of the atmosphere when the barometer stands at 29·905 inches at the sea-level in the latitude of London, the temperature being that of the freezing point. In order to know the pressure of the steam in which the thermometer is placed during the determination of the boiling point, a gauge is attached. This consists simply of a bent glass tube, open to the atmosphere at one end, and containing a little water. The difference of level of the water in the two arms gives the difference

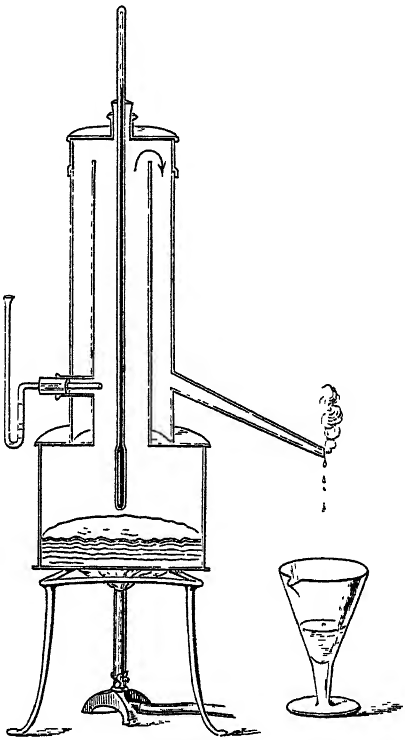


Fig. 8.

[1] In the apparatus used for determining the boiling point the vapour inside is usually and erroneously represented by clouds, and this perhaps fosters the idea commonly prevalent among beginners that steam is visible like a cloud. This mistake probably arises from the application of the word in ordinary language. Thus Robison, in his *Mechanical Philosophy*, vol. ii. p. 1, defines steam as "the visible moist vapour which arises from all bodies which contain juice easily expelled by heat. . . . It is distinguished from smoke by its not having been produced by combustion, by not containing any soot, and by its being condensible by cold into water, oil, inflammable spirits, or liquids composed of these. . . . The visibility of the matter which constitutes the steam is an accidental or extraneous circumstance, and requires the admixture with air, yet this quality again leaves it when united with air by solution." What we now term steam or vapour is an invisible substance, but when this condenses into small globules it becomes visible and is then called cloud, or mist, or water dust.

of pressure between the steam inside and the atmosphere outside the apparatus. If the escape orifice is large enough this difference will be scarcely sensible.

When the boiling point is marked the barometer will probably not be at the standard height, so that the mark made on the stem must not be regarded as the standard boiling point, and a corresponding correction must be made in graduating it. This correction will be found from tables of vapour tensions.

75. Graduation of the Thermometer.—The freezing and the boiling points having been marked, the interval between them may be divided into any desired number of equal parts. Each of these parts is called a degree, and hence we speak of a temperature being so many degrees above or below the freezing point. Three systems of division have been proposed, which are at present in general use. The centigrade scale was introduced by Celsius,[1] and is generally used in France and in all scientific work. In this scale the freezing point is marked 0°, and is called zero, and the boiling point is marked 100°, the interval between being divided into 100 equal parts.

The scale generally used by English-speaking people is that introduced by Fahrenheit,[2] of Dantzig, about 1714. In this scale the boiling point is marked 212° and the freezing point is marked 32°, the graduation extending above and below the fixed points. A point 32° below the freezing point is marked 0°, and is called zero. This point corresponded to the lowest known temperature in the time of Fahrenheit, namely, that of a mixture of snow and salt. The only arguments in favour of this scale are its early introduction and the fact that it is actually used by so many of our countrymen. A re-

[1] Professor of Astronomy in the University of Upsala.

[2] The view advanced in explanation of the mode of division of the Fahrenheit scale is that the interval between the freezing point and the boiling point was divided into 180 points like a semicircle. If this view has no foundation, it is certainly a strange coincidence that there should be on this scale exactly 180° between what are now taken as the two fixed points.

Professor A. Gamgee (*Proc. Camb. Phil. Soc.* 1890, vol. vii. pt. iii. p. 95) states that this view is nevertheless incorrect,—that Fahrenheit had settled the basis of his scale and constructed a large number of thermometers many years before the discovery by Amantons that water boils at a constant temperature under constant pressure. The thermometers first constructed by Fahrenheit were sealed alcohol-in-glass thermometers provided with a scale. The lower fixed point of the scale was determined by a mixture of snow and salt, and the upper by placing the thermometer under the armpit, or inside the mouth, of a healthy man. In the early thermometers the interval between these two fixed points was divided into 24 equal parts, and later on into $4 \times 24 = 96$. It was subsequently found that the 32nd degree corresponded to the melting point of ice, and the 212th to the boiling point of water. The basis of Fahrenheit's scale was then simply duodecimal division.

markable fact, however, is that mercury expands almost exactly $\frac{1}{10000}$ of its volume at 142° F. for every degree Fahrenheit, so that Young[1] defined the degree Fahrenheit as corresponding to an expansion of mercury equal to $\frac{1}{10000}$ part of its bulk.

The third thermometric scale is that of Réaumur. In this scale the freezing point is marked 0° and the boiling point 80°, the interval being divided into 80 equal parts. This scale is very generally used in Germany for domestic purposes, and possesses no advantages.

The relation between the readings of thermometers graduated according to these three methods is easily found, for 100 divisions of the centigrade scale are equal to $212-32=180$ divisions of the Fahrenheit and also equal to 80 of the Réaumur scale. Hence if C, F, R denote the readings of the three thermometers for the same temperature, we have

$$\frac{C}{100}=\frac{F-32}{180}=\frac{R}{80},$$

or

$$C=\tfrac{5}{9}(F-32)=\tfrac{5}{4}R.$$

From these equations, when the temperature is given by one scale, the corresponding number expressing the temperature on either of the others can be easily found.[2]

In the best modern thermometers the scale is marked on the glass stem of the instrument itself, but in most ordinary thermometers the graduations are made on a piece of wood, or ivory, or porcelain, to which the thermometer is securely attached. Some of the best ordinary thermometers (German bath thermometers) have the scale marked on a slip of paper which is enclosed in a glass tube hermetically sealed round the stem of the thermometer, and in this form the graduation is clearer and more easily read than in any other. The paper scale is completely protected from damp and damage by the sealed glass tube which encloses it. The lightness of the paper renders its attachment to the stem, by gum or otherwise, secure and trustworthy, and if the thermometer be never exposed to a temperature high enough to brown or injure the paper, it is cheaper and better than any other form of scale. The graduation on the glass of the stem itself is, however, superior to all others, except in respect to the ease of reading the divisions.

Lens front tubes are used for delicate thermometers of fine bore.

[1] Young, *Lectures on Nat. Phil.* p. 485.

[2] The scale called after Réaumur was proposed by De Luc (*Recherches sur l'atmosphère*, tom. ii. pp. 244-283). The true scale proposed by Réaumur marked 80 at the boiling point of alcohol, and consequently the boiling point of water on it differed little from 100°. It thus differed little from the centigrade scale.

The stem itself thus plays the part of a magnifying glass, and enlarges the bore about fifteen times.

76. Calibration of the Tube.—If it is agreed to measure equal increments of temperature by equal increments of the volume of some chosen substance contained in a glass envelope, it will be necessary to divide the stem of the thermometer into parts of equal capacity. Thermometer tubes are drawn and not bored, so that inequalities generally exist in the diameter of the capillary bore, and equal lengths will not have equal capacities from part to part of the tube. To test this a thread of about 20 or 30 mm. of mercury (Fig. 9) is placed in the tube and moved from part to part of its length. This may be conveniently effected by gently blowing into a piece of india-rubber tubing fastened to one end of the tube. In each position there will be slight

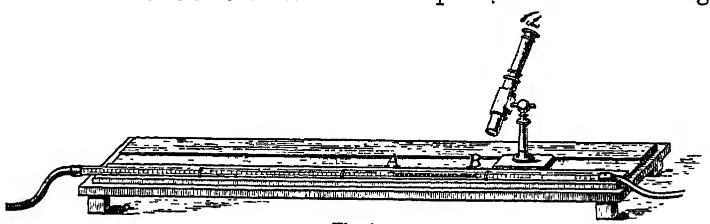


Fig. 9.

variations found in the length of the thread as it is moved from place to place, but if any considerable variation is detected the tube should be rejected and one of more uniform bore sought. In order to measure equal rises of temperature by equal increments of volume, it is necessary to know the capacity, or volume per unit length, of the stem, in terms of its capacity at some selected part. The process of effecting this is termed *calibration.*

One method often practised is to measure the length of the column in some chosen position AB, and then displace it into the position BC, the extremity which was previously at A now occupying the position B. By repeating this process the tube is divided into lengths l_0, l_1, l_2, etc., of equal capacity. Each of these lengths is again subdivided by the dividing engine into n parts, and each of these parts is called a degree. The division by this method, which is known as Gay-Lussac's step-by-step method, gives a scale which is discontinuous, each degree in the length l_0 being l_0/n, while those in the adjacent length l_1 are each of length l_1/n. This method of division, when well performed, is susceptible of considerable accuracy, and was used by Regnault, but the discontinuity of the scale is for many reasons objectionable, especially if at any time it is desired to again calibrate the instrument, when a troublesome correction will be necessary on account of the unequal

lengths of the degrees at different parts of the stem. The process of placing the thread so that the end shall be exactly at any given point is by no means easy, and it facilitates matters much, without diminishing the accuracy, if, instead of trying to bring the thread AB into the position BC, we simply bring the end A to a position A_1 (Fig. 10), fairly near B, and measure the error. Let this be x_{01}. Then if the length be l_1 in the position A_1B_1, we have $x_{01} = BA_1$, and the corrected distance of B_1 from A is $AB_1 - x_{01}$. This is the point to which the end A_2 of the thread must be brought in the third position A_2B_2, so that if $B_1A_2 = x_{12}$ the theoretic position of A_3 will be $AB_2 - x_{01} - x_{12}$, and so on. From this it will be seen that in the step-by-step process of division the errors are cumulative, and if they should happen to be all of the same sign a considerable error in the indications of the instrument may be ultimately introduced. In all cases, while the process of calibration is being carried out, the temperature of the tube should be kept uniform and constant in all parts; and the handling of the tube, or touching it with the hands on any part except the extremities, if it be necessary to move it, should be avoided.

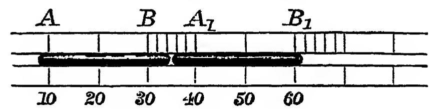


Fig. 10.

A preferable system is to first furnish the tube with a uniform millimetre scale, and then correct for inequalities of the bore, as well as for any want of uniformity which may exist in the scale. Errors of the latter sort are not unfrequent, and may arise either from some fault of the dividing engine, or from some external cause, such as a variation of temperature, or a displacement of the tube, during the process of division. To mark the scale the tube is first covered with a uniform film of engravers' varnish, and the lines are scratched on this with a fine steel point which lays bare the glass. The tube is then submitted to the action of hydrofluoric acid gas,[1] which attacks the glass where it is exposed along the scratches. This scale might also be marked directly on the glass by means of a diamond point, but lines drawn on glass in this manner are ragged in outline, and, besides weakening the tube, are sometimes so broad and uneven that it is difficult when viewing them through a microscope to fix with accuracy the point on the stem to which the centre of the mark corresponds. Engraving scale.

The calibration of such a tube is most easily performed before the bulb is attached, for in this case there is no difficulty in introducing, and moving about in it, a thread of mercury of any length desired. A

[1] The gas leaves a distinctly visible mark, but the liquid solution of the gas leaves a mark which is scarcely visible.

bulb may afterwards be blown on one end, or a previously-prepared bulb may be sealed to it. In all cases, however, the bulb should be made of the same glass as that which forms the stem, and for this reason it is perhaps better to blow the bulb on the tube either before or after calibration. In the former case the instrument is filled and sealed so as to be suitable for the range of temperature for which it is intended, and a thread of mercury of the proper length may be detached from the main mass in the bulb by holding the instrument vertically with the bulb upwards, and dexterously tapping the lower end on the table.[1] If the thread does not start, it can often be made to do so by alternately warming and cooling the bulb so as to pass the column to and fro in the stem. If the bore be very fine, great difficulty will often be experienced in detaching the thread, but a thread of any length desired may always be detached by heating the column in the tube at the desired point by means of a small gas flame,[2] when a so-called vacuum bubble will be formed at the point of application of the flame. By this means a thread may be detached to within 1 mm. of the required length. In all cases, however, the flame should be applied to a point of the tube outside the part which it is intended to calibrate, as the high heating may alter the bore of the tube, as well as the nature of the glass, at this place, both of which are most undesirable.[3] Sometimes, although there is no observable alteration in the bore, great difficulty is experienced in passing the thread past certain points. In a very fine tube such an obstacle may generally be passed by cooling the thread by means of a rag soaked in ether lapped round the tube, from which the ether is rapidly evaporating, and this same method may be employed in detaching the thread from the mass in the bulb.

Detachment of thread.

The measurement of the length of the thread at any part of the tube is made by means of a horizontal cathetometer, the tube being placed horizontally, or by means of a microscope movable in a horizontal slot parallel to the tube, so that it is possible to slide it along to view

[1] The separation of a thread is usually determined by a microscopic air-bubble adhering to the glass. If the mercury separates within the bulb, the bubble may be brought into the upper part of the stem by suddenly turning the thermometer upright. When this is done, the mercury will generally separate at the opening of the bulb, and consequently by warming or cooling the thermometer a thread of any length can be separated.

[2] The Committee of the British Association used a very small gas flame about 5 mm. long, issuing from a glass tube drawn out to a fine point. See Report for 1882.

[3] Professor S. U. Pickering (*Phil. Mag.* vol. xxi. p. 180, 1886) found that when the flame was applied to a point of the scale in calibrating the thread would run past this point at an ungovernable speed, while in the opposite direction it would scarcely pass at all.

any division of the stem. In this process a difficulty arises from the fact that the divisions on the outside of the stem, and the thread of mercury within, are at different distances from the object glass, and will consequently not be in focus at the same time, so that if the microscope is first adjusted to view the thread of mercury, and then moved till the scale is in focus, and the cross wire coincides with the nearest division of the scale, a change in the position of the line of collimation may occur which will render the reading inaccurate. To avoid this Mr. F. D. Brown[1] employed a split lens arrangement, by which both the scale and thread may be viewed at the same time, and the reading of the end of the thread made without altering the focus of the microscope. This consisted in placing a half lens before the object glass of the microscope, which had the effect of bringing the focus of half the field nearer the object glass. Hence, by properly adjusting the distance of the half lens, the scale may be seen through

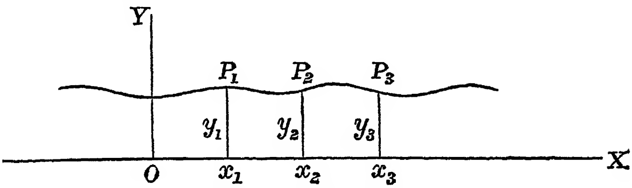


Fig. 11.—Calibration curve.

the half lens at the same time as the thread of mercury is viewed through the uncovered part of the object glass.

The end of the thread should not be placed under a scale mark, for the division lines are often ragged, and their width, even in the best scales, is a source of error, hiding the end of the thread so that its reading cannot be taken accurately. It is much better, therefore, to place the end of the thread beyond the scale mark, and to estimate its distance from the centre of the mark.

The length of the thread at any part of a tube, divided into parts of equal length, gives the mean capacity of each division at that part of the tube, so that by sliding the thread about in the tube, and measuring its length, the capacities of the various divisions may be tabulated and compared. This is most easily done graphically.[2] Thus if when one end of the thread, which we shall call the *near* end, is at the division x_1 (Fig. 11) its length is y_1, and if when the same end is at x_2 the length is y_2, and so on, then by measuring the lengths x_1, x_2, etc.,

[1] F. D. Brown, *Phil. Mag.* vol. xiv. p. 57, 1882.

[2] Silas W. Holman, *Proc. American Academy of Arts and Sciences*, vol. xvii. p. 157, 1881-82.

along a line OX, and erecting perpendiculars x_1P_1, x_2P_2, etc., we obtain a series of points P_1, P_2, P_3, etc., the co-ordinates of which, with respect to the axes OX and OY, are x_1, y_1; x_2, y_2; x_3, y_3, etc. By making a great number of measurements the points P can be brought as close together as desired, and a continuous curve will be formed by joining them together. This curve will give a general idea of the form of the bore (if any part of it shows great irregularity it should be again explored with the thread), and will be such that the ordinate (y) at any point is equal to the length of the thread when its near end is at the distance x from the point on the scale represented by O, and which may be chosen for the zero of graduation if desired. Hence, if the distance from x_1 to x_2 be equal to y_1, while that from x_2 to x_3 is equal to y_2, and so on, the intervals between x_1, x_2, x_3 will correspond to lengths of the bore which have equal capacities. If then the column is contained n times between any two points x_{n+1} and x_1, we have

$$x_{n+1} - x_1 = y_1 + y_2 + \ . \ . \ . \ + y_n.$$

Thus there are n parts of equal capacity between x_1 and x_{n+1}, and the capacity of each is $\frac{1}{n}$ that of the whole interval. Consequently, if the true reading at x_1 is x_1, then the true reading at x_2 is $x_1 + \frac{1}{n}(x_{n+1} - x_1)$, while the true reading at x_3 is $x_1 + \frac{2}{n}(x_{n+1} - x_1)$, and so on.[1]

Hence, since the error at x_1 is by supposition zero, the error at x_2 is the difference between the true reading $x_1 + \frac{1}{n}(x_{n+1} - x_1)$ and the scale reading x_2—

$$\text{error at } x_2 = x_1 + \frac{1}{n}(x_{n+1} - x_1) - x_2,$$

$$\text{error at } x_3 = x_1 + \frac{2}{n}(x_{n+1} - x_1) - x_3,$$

$$\text{etc.} \quad = \quad \text{etc.}$$

$$\text{error at } x_{n+1} = 0.$$

These results may be graphically exhibited by constructing a correction curve—that is, a curve whose abscissæ are the scale readings x_1, x_2, etc., and whose ordinates are the corresponding corrections. The corrections at the points x_1, x_2, x_3, etc., give a certain number of points, and a continuous curve can be drawn through them, the ordinates of which will give the corrections at all intermediate points.

[1] If the calibrating thread contains m degree measures, and if the volume of a degree measure be the mean volume of a scale division between x_1 and x_{n+1}, then obviously $mn = x_{n+1} - x_1$. But if x_1 is the true reading at x_1, then $x_1 + m$ is the true reading at x_2, etc.

Other correction curves may be constructed by starting from any other point of the scale, and by combining these increased accuracy will be obtained.

When two mercury thermometers are accurately calibrated it is found that their readings agree very closely at all points of the scale, provided they have been constructed in the same manner and of the same sort of glass; but if the glass be of different qualities in the two, or even if the glass be of the same quality but has suffered different treatment in the process of making the thermometers, it is found that the two generally differ, sometimes considerably, in their indications. It would appear, therefore, to no purpose to spend the necessarily great labour of calibration on any instrument save an air thermometer, which is chosen as the standard. All other instruments should be then merely graduated into divisions of equal length, and corrected by direct comparison with the standard air thermometer. Such a comparison may be obtained in this country for a small fee by sending the instrument to Kew.

77. Gradual Elevation of the Zero Point.—The first essential condition which must be fulfilled by a good thermometer is that it must always give the same reading when submitted again and again to the same temperature. Thus when placed in melting ice the reading should always be the same, no matter what variations of temperature the instrument has suffered, or how long the interval, between two such comparisons. For this purpose not only should the volume of the mercury be always the same at the same temperature, but glass should also satisfy this condition, or at least the apparent volume of mercury in glass should be always the same at the same temperature. This, however, is not the case. Glass when heated and allowed to cool does not immediately return to its original volume. It is in some degree plastic, and after it has been highly heated or strained a process of gradual recovery goes on for a long time afterwards. For this reason the reading of a thermometer depends not only on its actual temperature but also to some extent on the previous history of the glass. After a thermometer has been filled and sealed the capacity of the bulb gradually diminishes to a slight extent, rather rapidly at first, and then very slowly for years afterwards. In a few months, however, after the instrument has been filled and sealed, the recovery may be regarded as complete. For this reason the fixed points should not be determined until about six months after the process of filling, and it is then preferable to determine the freezing point before the boiling point, as the heating employed in the latter process produces a slight temporary enlargement of the bulb and

consequent depression of the zero point.[1] Thus it usually happens that after a thermometer has been constructed and the fixed points marked, a gradual shrinkage of the bulb takes place, and if tested after some time the new zero point will be somewhat above that previously determined. This displacement gradually increases if the thermometer is kept at a fairly uniform temperature, and may ordinarily amount to half a degree centigrade. A delicate thermometer possessed by Dr. Joule[2] was examined at intervals extending over a period of nearly forty years, and showed this gradual rise of the zero. The change, however, was exceedingly slow in the later years. Thirteen scale divisions corresponded to 1° F., and the reading of the zero point was found as follows, in scale divisions:—

Date.	Zero Reading.	Date.	Zero Reading.
April 1844	0	December 1860	11·1
February 1846	5·5	March 1867	11·8
January 1848	6·6	February 1870	12·1
April 1848	6·9	,, 1873	12·2
February 1853	8·8	January 1877	12·71
April 1856	9·5	November 1879	12·92
		December 1882	13·26

A delicate thermometer which has been kept for a long time at the ordinary atmospheric pressure, and never subjected to temperatures above 30° C., or much below the freezing point, remains very constant, and will probably never show a variation of more than a tenth of a degree in its freezing point or any other definite temperature between $+30°$ and $-10°$. The irregular variations caused by exposing a thermometer to temperatures much above or below some limited range forms a very serious difficulty in the way of accurate measurements by means of mercury thermometers, and although the utmost care has been bestowed by the greatest experimenters, such as Regnault and Joule, to avoid errors arising from this cause, we still possess little accurate information in thermometry regarding the effect of the different qualities of glass, the shape of the bulb, and process of construction by which the glass is blown, the bulb filled, and the stem sealed. The error due to this irregular shrinkage or enlargement of the bulb is obviously less the greater the expansion of the fluid with which the thermometer is filled. In fact, the error is very

[1] This gradual change of the zero point was first noticed by Flaugergues, *Ann. de Chimie et de Physique*, vol. xxi. p. 333, 1822.

[2] Joule, *Scientific Papers*, p. 558; *Phil. Soc.*, Manchester, 22nd February 1870.

nearly in the inverse ratio of the expansion of the fluid; consequently in this respect alcohol or ether is much superior to mercury, and a permanent gas is again superior to these.

The gradual displacement of the zero point has been supposed to be due to some extent to the pressure of the atmosphere on the external surface of the bulb under which the glass gradually sags. The effect of pressure on thermometer bulbs has been investigated by Egen[1] and Mills,[2] with the general conclusion that the displacement of the reading is proportional to the pressure. Mills employed pressures ranging up to 1·34 atm., but the thermometers he examined were not very delicate. The same subject was examined by Professor S. U. Pickering.[3] The thermometer bulb was enclosed in a thin brass cylinder connected with an air-pump, by means of which the pressure could be varied from zero to 2 atm. The case enclosing the bulb was filled with, and surrounded by, melting ice, and it was found that different thermometers deviated irregularly from the law laid down of Egen and Mills.

Effect of pressure.

When the bore of the stem of a thermometer is very fine its indications become complicated by the variation of the capillary pressure at different points of the tube. For this reason the internal pressure on the bulb may vary considerably, and corresponding errors in the indications of the instruments will arise. At some parts of the stem the mercury often experiences great difficulty in passing. At these points the mercury sticks, and then moves forward suddenly with a jerk. For this reason it does not seem desirable to use thermometer tubes of exceedingly fine bore. In falling the internal pressure is always less on this account than on rising, so that at a given temperature the reading will be slightly lower if the instrument has been rising to this temperature than if it had been falling. M. Crafts[4] found that thermometers which were kept for eleven days at 355° C., and were afterwards constantly used for two years and a half in experiments at all temperatures up to 326°, showed again, after being heated for half an hour to 355°, the same position of the zero to within 0°·1 C. He therefore considers that the permanent elevation of the fixed points produced at high temperatures preserves thermometers from the effects of heat in this respect at lower temperatures, and suggests that thermometers intended for laboratory work should be heated for a week or ten days to the temperature of boiling mercury before calibration and graduation.

Fine-bore tubes.

Permanent effect of high temperatures.

[1] Egen, *Pogg. Ann.* vol. xi. p. 283. [2] Mills, *Trans. Roy. Soc.*, Edinb., vol. xxix. p. 285.

[3] S. U. Pickering, *Phil. Mag.* vol. xxiii. p. 406, 1887.

[4] J. M. Crafts, *Comptes Rendus*, tom. xcv. p. 910, 1882. See also Heycock and Neville, *Proc. Camb. Phil. Soc.*, vol. vii. p. 319, 1892.

Professor Rowland [1] examined a thermometer which had remained in its case for four months at an average temperature of about 20° to 25° C., and after heating it to a definite temperature for a few minutes determined the zero point as soon as the instrument cooled, with the following result:—

Temperature before finding the Zero Point.	Change of Zero Point.	Temperature before finding the Zero Point.	Change of Zero Point.
22°·5	0	70°·0	−0·115
30°·0	−0·016	81°·0	−0·170
40°·5	−0·033	90°·0	−0·231
51°·0	−0·039	100° 0	−0·313
60°·0	−0·105	100°·0	−0·347

The second 100° reading was taken after prolonged boiling. The table shows that the lowering of the zero point increases as the temperature increases, being, within the limits of the table, approximately proportional to the elevation of the temperature above 25° C. This depression of the zero does not persist however at temperatures above 100° C., and above a certain point the phenomenon is reversed,[2] and the zero point is raised by heating.

After heating to 81° the zero gradually returned from −0°·17 to −0°·148 in two and a half hours, and after heating to 100° it returned from −0°·347 to −0°·110 in nine days, and to −0°·022 in a month. A thermometer which has not been heated above 40° should consequently be ready for use again in about one week.

78. On the Choice of a Thermometric Substance.—In respect to general convenience for a large variety of purposes, liquid-in-glass thermometers are with good reason preferred to all others, but the general preference for mercury or spirits of wine as the thermometric substance is not so clearly reasonable. The indications of a liquid thermometer depend both on the expansion of the liquid and on that of the glass envelope which contains it. If the glass and the liquid expand equally with rise of temperature, the apparent volume of the liquid in glass will remain constant. Since the indications of the instrument depend only on the difference of the expansions of the liquid and the glass, the greater the expansion of the liquid the more sensitive the thermometer, and for a given liquid the length of a degree

[1] H. A. Rowland, *Proc. American Acad. of Arts and Sciences*, vol. xv. pt. i. p. 82, 1879.

[2] Crafts found that in a thermometer heated for a few days at 355°, or a few hours at 430°, the zero point was raised 17° to 26°.

on the stem will be greater the larger the bulb and the smaller the bore of the tube. The high specific gravity of mercury limits the size of the bulb, for besides increasing the liability to break, the weight of the mercury strains the bulb and tends to give distorted readings, especially at high temperatures. Further irregularity is also introduced by the variations in the shape of the meniscus in the capillary tube.

Surface tension.

Besides the large value of the surface tension of mercury, the angle of contact varies from about 45° when the mercury is rising to 90° when it is falling. For this reason the internal pressure on the bulb is greater when the temperature is rising than when the temperature is falling, and a consequent variation in the volume of the bulb occurs which produces an irregularity in the indications of the instrument. On this account the mercury rises by jerks and not continuously when the temperature is increasing, and falls in the same discontinuous manner when the temperature is falling. This jerky motion of the mercury is very noticeable in delicate thermometers, and in some instruments is more so than in others. This Joule believed to be due largely to the slight oxidation of the mercury before sealing.

Liquids which wet the glass have a great superiority over mercury in their much smaller surface tension and in their practically constant angle of contact (180°). The variations of internal pressure are thus much less when the liquid is rising or falling and the motion in the tube is continuous. The large expansion of such liquids as alcohol, ether, chloroform, etc., gives the instrument in addition a great sensibility, and they possess a further great advantage over mercury in their much smaller specific gravity, so that larger bulbs may be used with consequent greater sensibility, and less liability to break or produce disturbed readings through distortion of the bulb by the weight of the liquid.

One objection to alcohol and other volatile liquids is their liability to distil into the head reservoir of the stem if this part of the instrument is colder than the bulb. On this account the stem of a spirit thermometer should be at least as warm as the space in which the bulb is situated. In practice, however, little difficulty is experienced in arranging that the part of the stem above the surface of the liquid shall be as warm as, or warmer than, the spirit, and this will suffice to prevent distillation.

The only serious objection to liquids of high expansibility is the difficulty of allowing for the expansion of the liquid in the stem if it be not at the same temperature as that in the bulb. The error arising from this cause will, under the same conditions, be proportional to

the expansibility of the liquid, but in every case in which the bulb and stem can be kept at the same temperature, a thermometer constructed with a highly expansive and light liquid, such as alcohol or ether, or other organic liquid of permanent chemical constitution, must be much more accurate and sensitive than one filled with mercury. The low boiling points of these liquids render them unfit for the construction of thermometers which are to be used at high temperatures, but for low temperature they make very valuable instruments. A sulphuric ether thermometer was employed by Lord Kelvin in his experiments on the lowering of the freezing point of water by pressure, and thermometers filled with ether or chloroform (which expands 4 % more than ether) were used by Joule and Thomson in their experiments on the change of temperature of bodies moving in air. In one of these thermometers there were as many as 330 scale divisions to 1° C.

Another objection frequently urged against spirit thermometers, but which does not appear to have any weight, is that when the temperature is rapidly falling a thin film of the liquid lags behind adhering to the sides of the tube, so that before the stationary temperature can be correctly read it is necessary to wait some time to allow the liquid to trickle down and join the main column. Adaptability to the measurement of rapidly-varying temperatures would thus seem to be wanting. With mobile liquids, such as alcohol and ether, there will, however, be practically no time lost on this account, and when proper care is exercised by the observer no inaccuracy will be incurred.[1] When the temperature has been rapidly falling, and has nearly reached its lowest point, a false balance must be guarded against, which arises from the descent of the liquid surface due to fall of temperature being counterbalanced by the rise caused by the liquid trickling down from the sides of the tube. This may give a false steadiness when the free surface has nearly reached the true position for the final temperature.[2]

The great convenience of the mercury thermometer is its freedom from distillation and the smallness of the error arising from any difference between the temperature of the bulb and that of the stem. It is further well suited to the measurement of ordinary temperatures, the boiling point of mercury being 350° C., and its freezing point 40° C. below the freezing point of water. For these reasons it is well suited for a large variety of practical purposes in which minute accuracy and extreme delicacy are not required.

The ultimate standard for thermometry is, for reasons which will

[1] Sir Wm. Thomson, *Math. and Phys. Papers*, vol. iii. p. 142.

[2] For the graduation of spirit thermometers see a note by M. A. Angot, *Journal de Physique*, Sept. 1891.

appear later, afforded by the use of a permanent gas, such as hydrogen or nitrogen, for the thermometric substance, but these gas (or air) thermometers are exceedingly inconvenient and troublesome in use. In practice highly sensitive thermometers constructed of some chosen organic liquid, and graduated by comparison with a standard air thermometer, seem the most accurate and convenient.

79. Overflowing Thermometers.—In ordinary liquid-in-glass thermometers the expansion is noted by the rise of the liquid in a tube divided into parts of equal or known capacities. The same result may be also attained by allowing the liquid to overflow, and determining the volume of the overflow by weighing. This is the method practised in what is known as the *weight thermometer*, and the difficulties attending the calibration and change of zero of the ordinary thermometer are thus avoided. This instrument consists of a glass bulb capable of containing about 200 grammes of mercury, which is furnished with a short capillary tube, and filled at zero in the ordinary way and weighed. Let W_0 be the weight of mercury which fills the instrument at the freezing point, w the weight which overflows at any temperature θ. Then w is the apparent expansion of a weight $W - w$ of mercury in rising from $0°$ to $\theta°$; consequently if a denotes the apparent expansion of mercury in glass, we have

Fig. 12.

$$(W - w)a\theta = w,$$

or

$$\theta = \frac{w}{(W - w)a}.$$

To determine a it is only necessary to make an experiment at 100° C., which gives

$$a = \frac{w_{100}}{100(W - w_{100})}.$$

This coefficient varies with the nature of the glass, and it is therefore necessary to determine it directly for each instrument (see also p. 175).

80. Maximum and Minimum Thermometers.—Thermometers for registering the highest or lowest temperature attained during any interval may be devised in several ways. Thus the weight thermometer may be arranged as a maximum thermometer, for if the mercury as it overflows is allowed to drop into a cup, the quantity expelled in any time gives the highest temperature reached by the instrument during that period. This, in fact, is the principle of Walferdin's maximum thermometer.

The ordinary mercury thermometer will, however, serve as a maximum thermometer if a small iron index is placed in the tube so as

to move before the surface of the mercury. As the mercury expands the index is pushed before it in the stem, and when the temperature falls the index is left behind. The position of the index at any time thus gives the highest temperature that has been attained since the instrument was last set. This is the principle used in Rutherford's maximum and minimum thermometers (Fig. 13). The two thermometers are attached to a frame with their stems directed horizontally. One of these thermometers registers the maximum temperature, and the other the minimum. The former is an ordinary mercury thermometer furnished with a light steel index which is movable in the stem, and can be brought to the surface of the mercury by means of a magnet when it is desired to set the instrument. The reading of that end of the index which is next the surface of the mercury at any other time gives the maximum temperature attained since the instrument was last set. The minimum temperature is registered by the other thermometer. This is a spirit thermometer, and is furnished

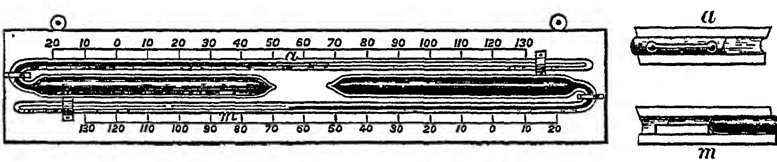


Fig. 13 —Rutherford's.

with a light dumb-bell-shaped enamel or glass index, which is generally coloured. When the spirit expands it flows past the index without displacing it, but when the temperature falls, and the surface of the spirit reaches the index, the latter is retained by the capillary action of the surface and is carried back in its grasp. As the surface recedes, the end of the index, which is directed away from the bulb, marks the temperature, and at any other time this end of the index marks the lowest temperature attained. Thus in each thermometer that end of the index which is directed towards the surface of the liquid marks the highest or lowest temperature attained.

Six's self-registering thermometer is one of the oldest of this class of instruments, and acts both as a maximum and minimum thermometer. It is shown in Fig. 14, and consists of one continuous tube, the two ends of which contain alcohol[1] (or creosote), and the

[1] Alcohol after some time evolves small bubbles of air which give trouble. Sulphuric acid would probably serve better. Herr von Lupin of Munich recommends dilute sulphuric acid and a solution of 10 or 15 per cent of anhydrous calcium chloride in spirit as liquids free from distillation errors and possessing regular expansion (*Nature*, 1893, p. 206, 29th June).

intermediate space is filled with mercury. The large cylindrical bulb A is also filled with alcohol. The part BC contains mercury, and above C there is some more alcohol, which also partly fills the bulb D, some space being left for expansion. Thus both extremities of the mercurial column are in contact with alcohol, and situated in the alcohol above the mercury, in each arm, is a light steel index which is held in its place by a delicate spring, just strong enough to prevent slipping down the tube. When the alcohol expands in the bulb A the mercury rises in the left arm, and pushes the index before it, leaving the index in the right arm behind in the alcohol; and when the temperature falls the liquid contracts, and the mercury rises in the right arm, pushing the index in this arm before it and leaving the other behind. Thus the index in the left arm gives the maximum, and that in the right gives the minimum, temperature.

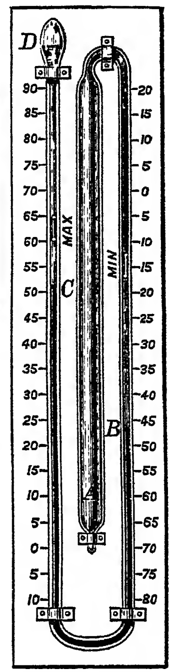


Fig 14.—Six's.

In the maximum thermometer of Negretti and Zambra there is an obstruction in the tube close to the bulb, so that the bore is nearly choked at this point. As a consequence, the mercury expanding in the bulb forces its way past the obstruction into the stem above; but, on the other hand, when the temperature falls, the thread of mercury beyond the obstruction in the stem fails to make its way back again into the bulb. This isolated thread furnishes the means of determining the highest temperature reached by the instrument since it was last set, for when one end of the thread is placed against the obstruction, the other end gives the maximum temperature—a correction being applied for the expansion of the thread if extreme accuracy be desired. In setting this thermometer, the thread of mercury in the stem is shaken past the obstruction till it joins the main mass in the bulb, and the instrument is now ready for another observation.

Negretti and Zambra.

Fig. 15.

Fig. 16.

Clinical.

The same principle is adopted in the clinical thermometers now generally used. These instruments (Fig. 15), being employed to register only a very limited range of temperature, are furnished with a very open scale graduated from 95° to 113° F., so as to include the variations of temperature to which the sick are subject. In order that the scale may be open, the bore of the tube is made very fine, and the reading is facilitated by the use of a lens-front stem, so that the thread of mercury is magnified, and the employment of a pocket lens is thus dispensed with. The employment of the latter is besides attended by difficulties in ordinary instruments as already mentioned, on account of difference of focal distance of the thread and scale.

Phillips.

Another form of maximum thermometer is that invented by Professor Phillips. In this instrument the bore is exceedingly fine, and the thread of mercury in the stem is broken by a small air-bubble. The portion of the thread above the bubble serves as an index which is pushed before the bubble when the temperature is rising, but remains *in situ* when the temperature falls. This index is not easily shaken out of its place, and with a very fine bore the instrument may be used with the stem vertical, as in Fig. 16 which represents a Phillips' thermometer enclosed in a strong glass tube as designed by Lord Kelvin for the observation of deep-sea temperatures. The enclosing tube is hermetically sealed and protects the thermometer from outside pressure, to which it would otherwise be subject. In the lower part of the case a small quantity of spirit surrounds the bulb which places it in better thermal communication with the outside medium.

Deep sea.

SECTION II

GAS AND VAPOUR-PRESSURE THERMOMETERS

81. **Gas Thermometers.** — The indications of mercury thermometers are complicated by certain effects due to inequalities in the expansion of the glass envelope, which depend not only on the temperature, but also on the previous history of the glass. The influence of the nature of the glass on the indications of the instrument will become less and less the greater the coefficient of expansion of the contained liquid. In this respect thermometers filled with highly expansive organic liquids will be superior to those filled with mercury, and air or permanent gas thermometers will be superior to the most accurate liquid thermometers. The permanent gases expand about twenty times as much as mercury for the same change of temperature, and as a consequence the errors arising from inequalities in the expansion of glass are less than those which must inevitably accompany experimental observation. Gases also possess a very low specific gravity, and can be obtained of the same purity in any part of the world. Their properties are in addition permanent (at least in the case of hydrogen[1]), and they all expand equally under the same conditions, so that thermometers filled with different permanent gases all agree very closely amongst themselves.

No two solids or liquids, on the other hand, can be found which will agree throughout the scale, and in absence of any other reason for choosing a permanent gas as the standard thermometric substance, the close agreement of so many different substances throughout such a wide range of temperature attaches great practical importance to the scale of temperature furnished by their expansion. The permanent gases besides, when not subjected to too great pressure, maintain their state and behave in the same manner (at least very approximately) at the highest as well as the lowest temperatures yet attained. They consequently furnish a scale of measurement

[1] See footnote to Art. 49.

of temperature which is continuous and embraces all temperatures yet experienced.

The uniformity of composition of the atmosphere all over the world, combined with its cheapness and the ease with which it can be obtained, has led to the employment of air, as a permanent gas, for thermometric purposes. Precautions of the strictest character are, however, taken to remove all moisture and other variable impurities, such as carbonic acid, from any sample used in a thermometer. This is effected by passing the air through a system of tubes containing calcium chloride, pumice-stone moistened with sulphuric acid, and caustic soda, the former to absorb the aqueous vapour and the last to take up any carbonic acid gas which may be present. The removal of moisture is of prime importance, as a small quantity of aqueous vapour, although of small influence at low temperatures, might have a very serious effect on the indications of the instrument when the temperature becomes high. On this account the bulb is filled (and emptied) several times with perfectly dry air, and at the same time heated to a high temperature to expel all moisture which may be condensed on the interior surface or lurking in the minute crevices or pores of the glass. When every precaution has been taken to thoroughly dry the interior of the bulb, it is finally filled at 0° C. with pure dry air, or other gas as desired.[1]

Constant pressure or constant volume.

The instrument may now be used to measure temperature in two ways—(1) by change of volume while the pressure is kept constant; (2) by change of pressure while the volume is kept constant. Regnault used both methods, but found that in practice he could only arrange the apparatus to give good results with the second method, and on it he founded what he called the "normal air thermometer." For the sake of perfect definiteness he chose as the density of the air in his normal thermometer the density of air at the melting point of ice and under a pressure of one standard atmosphere, and he marked the freezing and boiling points 0° and 100° in accordance with the centigrade scale. We shall now prove that the second method agrees with the first in the case of a substance which obeys Boyle's law.

[1] A gas should be chosen which does not attack the other materials used in the construction of the instrument. Pure oxygen is objectionable on this account, as it attacks the mercury employed to measure the pressure of the gas. A film of oxide is formed on the surface of the mercury, and this is not only detrimental to the free motion of the mercury in the tube, but the whole quantity of oxygen in the bulb becomes diminished, and the readings of the instrument are influenced accordingly. For this reason hydrogen and nitrogen are preferable to air. Regnault, however, does not appear to have experienced any ill effect in this direction from the use of air in his normal air thermometer, but he found great irregularities with pure oxygen (*Expériences*, tom. i. p. 77).

82. Characteristic Equation of a Thermometric Substance obeying Boyle's Law.—If the first system of thermometry be adopted, we measure equal changes of temperature by equal changes of volume of the thermometric substance under constant pressure. The difference between any two temperatures θ and θ_0 will, therefore, be proportional to the difference between the corresponding volumes v and v_0, or

$$\theta - \theta_0 = \mathrm{A}(v - v_0).$$

In this equation the constant of proportionality A is independent of both temperature and volume, and is consequently a function of the pressure only. It remains constant as long as the pressure is constant, but changes value in general with the pressure. Denoting it by $f(p)$, the equation connecting the temperature, pressure, and volume of the thermometric substance, whatever it be, is

$$\theta - \theta_0 = (v - v_0)f(p).$$

When θ_0 and v_0 are chosen the right-hand member of this equation remains constant at the same temperature, however the pressure and volume may vary. It is therefore the isothermal relation between the pressure and volume of the substance, and gives the law of compressibility at constant temperature.

If the zero of temperature be taken as that at which the volume of the substance is zero (for the present ideal only), then writing $\theta_0 = 0$, and $v_0 = 0$, and denoting the temperature measured from this zero by Θ, the equation becomes

For any thermometric substance.

$$\Theta = vf(p).$$

The right-hand member being a function of p and v, which remains constant at constant temperature, will, in the case of a substance obeying Boyle's law, be simply some multiple of pv; we may therefore write

$$pv = \mathrm{R}vf(p),$$

where R is a constant. This gives in the case of a gas

$$f(p) = \frac{p}{\mathrm{R}},$$

and consequently the characteristic equation becomes

$$pv = \mathrm{R}\Theta,$$

For a gas.

where Θ is the temperature measured from the zero defined above.

This equation holds for a thermometric substance obeying Boyle's law, and follows immediately from the definition of the manner in

which temperature is measured. If another thermometer be constructed with another substance which also obeys Boyle's law, a similar equation will connect the pressure, volume, and temperature registered by this instrument, but we cannot assert *a priori* that the zero of temperature will be the same for both, or, in other words, that the volumes will vanish simultaneously in the two instruments, that is, that they both have the same coefficient of expansion. Such an agreement must be discovered by experiment, and that it does exist, at least very approximately in the case of the permanent gases, was discovered by Charles and Gay-Lussac, and is stated in the law which bears their names. Assuming it to be true for the present, we conclude that the above equation holds for all gases in so far as they obey Boyle's law, the zero of temperature being that at which the volume of the gas would vanish under constant pressure if it continued to obey the law throughout the whole range.

Law of Charles.

The equation also shows that if the volume is kept constant while the pressure and temperature vary, the change of temperature will be proportional to the change of pressure, and that consequently the second method of measuring temperature, or difference of temperature, is consistent with the first, and that two thermometers, filled with a substance obeying Boyle's law, will agree throughout the scale in their indications if the temperature is measured by change of volume under constant pressure by one, and by change of pressure at constant volume by the other. In the latter case the zero of temperature is that at which the pressure becomes zero while the volume is kept constant, and this aspect recommends itself especially on the dynamical theory, according to which the pressure is caused by the molecular bombardment. The meaning of the pressure becoming zero, according to this theory, is that the molecules come to rest relatively to each other. Hence, if the energy of translation of a molecule happens to be proportional to its energy of vibration or internal energy, or if the vibratory motion of the molecule subsides with its motion of translation, then when the pressure is zero there is complete relative rest in the gas. In other words, it is not a source of heat waves, and consequently may, with definiteness of meaning, be said to be at the absolute zero of temperature.

This view of the absolute zero appears at first sight more rational than the former, by which it was defined as the temperature at which the volume vanishes. However, both are based on the pressure volume relation at constant temperature known as Boyle's law, which asserts that the volume is inversely as the pressure for all values of the pressure—that is, that the thermometric substance maintains this

characteristic permanently. Such, however, is not the case with any substance that has been experimented on, but with permanent gases it holds very closely within moderate ranges. An ideal substance, named a perfect gas, has consequently been assumed which possesses these characteristics at all pressures. In other words, a perfect gas is a substance which always obeys the laws contained in the equation

$$pv = R\Theta,$$

and the temperature registered by a thermometer filled with this ideal substance is called absolute temperature. Thermometers filled with air, or nitrogen, or hydrogen, approximate very closely in their indications to this ideal instrument within a considerable range.

83. Constant Volume and Constant Pressure Air Thermometers.—The great objection to a constant pressure air thermometer lies in the temperature correction which must be applied to that part of the air which occupies the stem of the instrument. This correction will always be necessary, unless the bulb and all that part of the stem occupied by air are immersed in the same bath, and its influence will manifestly be more and more important as the temperature rises, and as more and more air is expelled from the bulb into the stem, so that the mass of air contained in the stem becomes comparable with that enclosed by the bulb. For this reason it is almost impossible to work with a constant pressure air thermometer, and after repeated trial Regnault found that he could only obtain consistent results with gas thermometers when they were arranged so that the gas was kept at constant volume, and the temperature was measured by the variation of the pressure.

The form of apparatus adopted by Regnault is shown side and front view in Fig. 17. The bulb A, which has a capacity of from 600 to 800 c.c., is filled with pure dry air (or other permanent gas), and is connected to a manometric tube FGHIJ. When the temperature varies mercury is poured into the branch IJ, or allowed to escape through the tap K, so that the level[1] of the mercury in the branch FG is kept always at a fixed mark α. If the glass were non-expansive the volume of the air would thus be kept always the same, but on account of the expansion of the glass a corresponding correction becomes necessary. The difference of level between the surfaces α and β in the two arms may be measured by means of a cathetometer, and the corresponding pressure of the air in the bulb deduced.

[1] The pouring of mercury into the tube IJ may be conveniently avoided by forming a reservoir at K, and furnishing it with a screw plunger. By screwing the plunger forwards or backwards the level of the mercury may be adjusted as desired.

If it is desired to work under constant pressure the difference of level between the surfaces α and β must be kept constant; consequently when the temperature rises the air expands into the tube FG and the volume and temperature of this expelled portion must be accurately determined. For this purpose the arm FG is accurately calibrated and immersed in a bath, as shown in Fig. 18, so that its temperature may be maintained uniform.

A convenient form of constant volume air thermometer has been

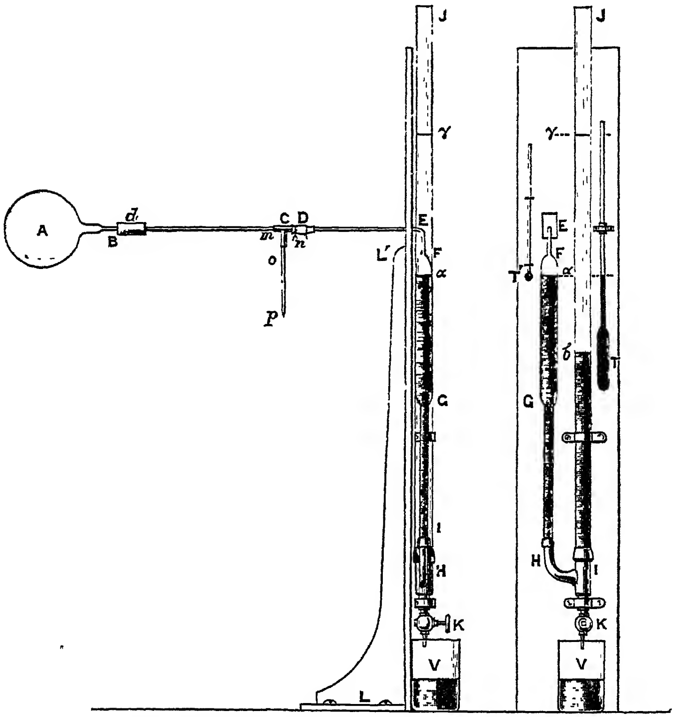


Fig. 17.—Regnault's Constant Volume Air Thermometer.

devised by Professor Jolly,[1] and is represented in Fig. 19. The capillary stem is bent twice at right angles, and united at B to a tube of larger bore, on which a fixed mark is placed near the junction of the capillary. In all measurements the level of the mercury contained in BD is brought to this fixed mark, so that the volume of the air in the bulb and stem is constant if we neglect changes of volume of the glass envelope. CE is a glass tube, preferably of the same diameter as B, to avoid difference of capillary pressure influencing the

[1] Jolly, *Pogg. Jubelband*, p. 82, 1874.

results. If, however, the diameters of the tubes be fairly large this effect will be negligible, and the tube CE may be replaced by a spherical bulb. The tubes B and C are joined by an india-rubber tube, which is strong and flexible, and allows CE to be raised or lowered so as to keep the level of the mercury at B. The difference of level of the mercury at E and B, added to the barometric height, gives the pressure of the air in the thermometer. This difference of level may be obtained by means of a cathetometer, but for ordinary

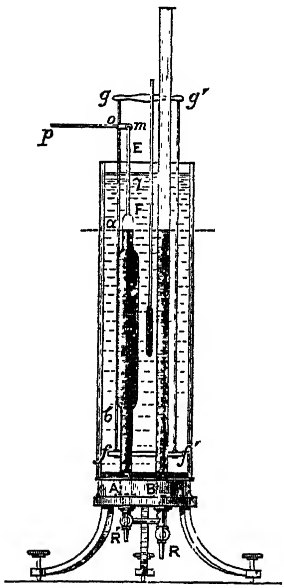


Fig. 18.
Constant Pressure Air Thermometer.

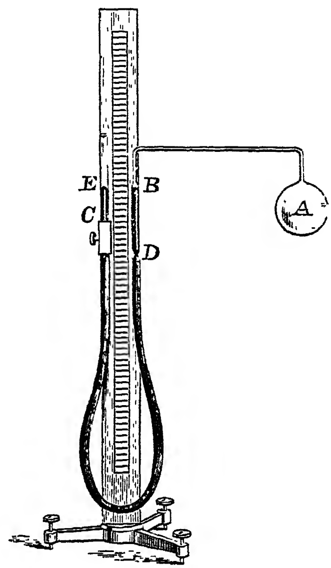


Fig. 19.
Jolly's Air Thermometer.

work a scale attached to the frame on which the instrument is mounted suffices. The scale is engraved on the back of a strip of plane mirror before it is silvered, and the divisions are carried sufficiently far across the scale for the reflections of the two surfaces of mercury to be seen behind the scale. Parallax is thus avoided, and the use of the cathetometer dispensed with.

Assuming the internal volume of the thermometer to remain constant, and that the temperature of the air throughout is the same, we have for any two temperatures Θ_0 and Θ_1

$$p_0 v = R\Theta_0, \qquad \text{and } p_1 v = R\Theta_1.$$

Therefore

$$\frac{p_1}{p_0} = \frac{\Theta_1}{\Theta_0}.$$

If such an instrument be graduated so that the boiling point is denoted by 100°, and the freezing point by 0°, then

$$100 = \Theta_{100} - \Theta_0 = \frac{v}{R}(p_{100} - p_0).$$

According to the most accurate observations of Regnault

$$p_{100} = 1 \cdot 3665 p_0,$$

and therefore

$$\frac{v}{R} = \frac{100}{0 \cdot 3665 p_0} = \frac{272 \cdot 85}{p_0}.$$

Consequently, any temperature θ on this scale will be given by the formula

$$\theta = \Theta - \Theta_0 = \frac{v}{R}(p - p_0) = 272 \cdot 85\left(\frac{p}{p_0} - 1\right).$$

In general, however, the volume of the glass envelope will vary, and the temperature of the air in the stem will differ from that in the bulb, and corrections will be necessary in both respects. These corrections will be considered more fully in connection with the general problem of dilatation. The source of greatest uncertainty in gas thermometers lies in the allowance for the expansion of the glass. This requires the careful examination of the volume of the bulb and tube throughout the whole range of temperature for which the instrument is to be employed. The volume of any such apparatus is most accurately determined by observing the weight of mercury which it contains at different temperatures, and when the variation of the density of mercury with temperature is known the volume can be immediately determined. This, in fact, was the process adopted by Regnault.

Jolly's constant volume air thermometer is a convenient form, and fairly accurate for moderate temperatures. At high temperatures, however, a correction becomes necessary on account of the air expelled from the bulb into the capillary tube. If the temperature of the bulb were always the same as that of the tube, the mass of gas contained in the tube would be constant; but as the tube is colder than the bulb, at high temperatures the pressure will be largely increased, and a corresponding increase will take place in the mass of gas contained in the tube. In order to minimise the error which arises in this respect, Dr. Bottomley[1] has designed a form of apparatus in which the air reservoir with its volume indicator and the manometer are constructed separately, and connected only by flexible tubing. The form given to the air bulb and capillary tube

[1] J. T. Bottomley, *Phil. Mag.*, August 1888, p. 149.

is such that it can be easily manipulated and constructed of hard Bohemian glass, and the range of the instrument is thus considerably extended.

An objection to all forms of constant volume thermometers exists in the pressure of the gas on the internal surface of the bulb, and this becomes more serious at high temperatures. By starting with a very low internal pressure this may, however, be obviated to some extent.

84. Callendar's compensated Air Thermometer.—The great practical difficulties attending the use of the constant pressure air thermometer have been overcome in the form of apparatus devised by

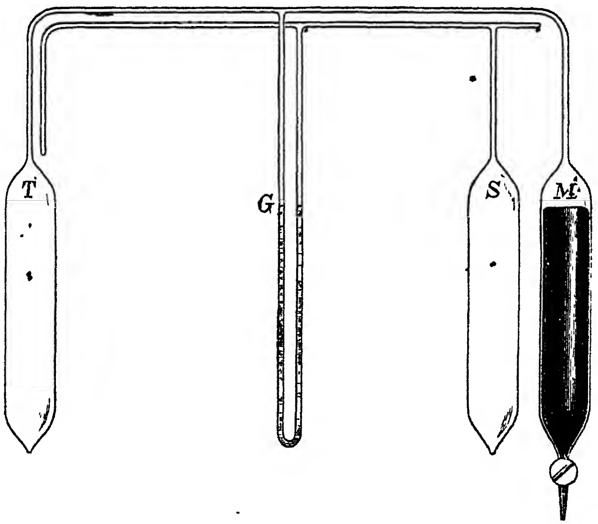


Fig. 20.

Mr. H. L. Callendar.[1] In this instrument the pressure of the air enclosed in the thermometer bulb T (Fig. 20), instead of being adjusted to equality with the pressure of the atmosphere, is maintained constantly at the same standard pressure as that of the air in another bulb S kept at a constant temperature in melting ice, the equality of the pressures in T and S being indicated by a sulphuric acid gauge G. By this means the trouble of reading the barometer is completely avoided, and by a most ingenious device the errors arising from the uncertainty of the temperature of the connecting tubes are compensated for and entirely eliminated. When the temperature of the thermometer bulb T rises, the air expands and passes through the

[1] H. L. Callendar, *Proc. Roy. Soc.* vol. l. p. 247, 1891.

narrow connecting tube into the mercury reservoir M. The quantity of mercury in M is adjusted, so that the pressure in T is equal to that in S, any difference of pressure being indicated by the sulphuric acid gauge G, which connects S and T. The bulb S being kept in ice the pressure of the air within it remains constant, and when the gauge shows that equality of pressure exists between T and S, it is certain that the pressure in T is always adjusted to the same value.

The correction for the capacity of the tube joining T and M is eliminated by attaching to S an exactly similar tube (as shown in figure), which has the same form and capacity, and which is placed close to it, so that the two have the same mean temperature throughout. By this means the compensation is rendered automatic, and will be perfect if (1) the two sets of connecting tubes have the same capacity, and are at the same mean temperature; (2) if the mass of air in the standard pressure bulb S is equal to that in the thermometer bulb T and the mercury bulb M combined; (3) if the pressures in T and S are adjusted to equality.

Thus if m be the total mass of air in T and M and the connecting tube and p its pressure, and if θ be the temperature of T on the scale of the air thermometer and v its volume, while θ_1 and v_1, θ_2 and v_2 are the corresponding quantities for the connecting tube and the air space in the bulb M respectively, we have by the law of Charles

$$p\left(\frac{v}{\theta}+\frac{v_1}{\theta_1}+\frac{v_2}{\theta_2}\right)=m\mathrm{R},$$

where R is a constant. In the same manner, if v' denotes the volume of S and v_1' the volume of the tubes attached, m' the total mass of air contained, p' the pressure, and θ' and θ_1' the corresponding temperatures, we have for this system

$$p'\left(\frac{v'}{\theta'}+\frac{v_1'}{\theta_1'}\right)=m'\mathrm{R},$$

so that if $m=m'$, and $p=p'$, and if the temperatures θ_1 and θ_1' and the volumes v_1 and v_1' of the two sets of connecting tubes are the same, we have

$$\frac{v}{\theta}+\frac{v_2}{\theta_2}=\frac{v'}{\theta'}.$$

If M and S are both kept in melting ice, we have further $\theta_2=\theta'=\theta_0$, and hence

$$\theta=\theta_0\frac{v}{(v'-v_2)},$$

or writing T, S, M, for the volumes of the air in these bulbs the

formula becomes $\Theta = \Theta_0 T/(S - M)$, so that the influence of the connecting tubes is completely eliminated.

The volume of the standard pressure bulb S may also be adjusted at pleasure by means of mercury, and in this manner the pressure may be varied and the behaviour of the gas investigated at high temperatures, and the indications of the instrument reduced to the absolute scale of temperature (Chap. VIII., Sec. iii.).

If the volume of the connecting tube is small compared with that of the bulb T, a small difference of pressure will not lead to any serious error, and on account of the compensating tube the connecting tube may be made long and flexible, and the bulb T may be placed at a convenient distance from the indicating apparatus, which is a matter of great convenience in many operations.

For moderate ranges of temperature the auxiliary bulb M may be dispensed with, and the sulphuric acid gauge G may be graduated so as to indicate the difference of temperature between T and S directly. In ordinary use it would be inconvenient to keep the bulb S always at a fixed temperature, and this may be avoided by adjusting the volume of sulphuric acid in the pressure gauge, so that its expansion may compensate for the dilatation of the air in the standard pressure bulb, a compensation which can be effected with sufficient accuracy for moderate ranges of temperature. Such thermometers, Mr. Callendar states, are "exceedingly convenient and satisfactory for rough work at temperatures beyond the range of mercury thermometers. They can be made to read easily to the tenth of a degree at 450° C., and if properly compensated their indications are very reliable. Such a degree of accuracy is amply sufficient for most purposes, and the absence of all necessity for calculation or correction of the readings is a very great advantage."

85. Vapour-pressure Thermometers.—A system of thermometry in which all delicate measurements of change of volume are avoided may be founded on the observation of the pressure of a saturated vapour. The pressure of a vapour in contact with its own liquid depends only on the temperature, and is independent of the relative proportions of liquid and vapour. If, therefore, the pressure is observed by some means, and if the data are known which connect the pressure with the temperature, we are furnished with a thermometric method of great range and delicacy. A simple form of vapour-pressure thermometer is shown in Fig. 21. The bulb is partly filled with a liquid free from air, and the remainder of the bulb is occupied by its saturated vapour. The liquid also partly fills the tube and acts as a manometer, the pressure of the vapour in the bulb

being greater than the pressure at the upper surface by the weight of the column of liquid, whose height is equal to the difference of level of the liquid in the bulb and tube respectively. If the stem is closed, and contains only vapour of the liquid above the upper surface, the pressure will be determined by the temperature of this part of the apparatus. For this reason the stem must be jacketed with a bath kept at some known temperature, say that of melting ice. The vapour-pressure in the stem is by this means kept constant, and the temperature and density of the liquid in the stem are also kept uniform, as well as the surface tension of the liquid.

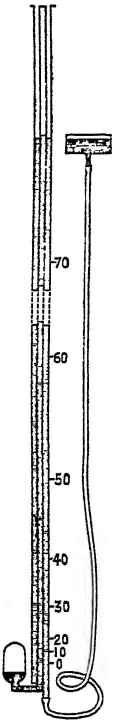


Fig. 21. Vapour-pressure Thermometer.

The stem may, however, be open at the top, and the pressure determined by a reading of the barometer, or it may be closed and contain a gas whose compression registers the pressure, or it may be connected to any form of pressure gauge.

For high temperatures mercury may be employed as the thermometric substance, and for low temperatures sulphurous acid, but in all cases the bulb must be made of a material which is not attacked by the vapour or liquid. For example, water vapour vigorously attacks glass at elevated temperatures.

The importance of this system of thermometry has been insisted on by Lord Kelvin,[1] who considers it destined to be of great service, both in the strictest scientific thermometry as well as in a great variety of useful applications. The consideration of the data necessary to the estimation of temperature by this method will be entered into later on (see Chap. VIII.).

86. Comparison of Thermometers.—The value of a gas thermometer as a standard depends upon the fact that two gas thermometers constructed in the same manner agree in their indications. This important property has been established by the accurate and laborious researches of M. Regnault.[2] Besides his normal air thermometer, M. Regnault constructed others in which the pressure at the freezing point was about one-half an atmosphere (438 mm.) and two atmospheres (1486 mm.) respectively, and determined the mean coefficient of expansion between 0° C. and 100° C. by the ordinary process of observing the volume, first when immersed in melting ice, and then

[1] Art. "Heat," *Ency. Brit.*

[2] *Mémoires de l'Académie*, tom. xxi., Paris, 1847.

in the steam of boiling water. These thermometers were then placed with the normal air thermometer in the same bath, the temperature of which could be varied at pleasure, and it was found that their indications were the same, or differed by quantities which were negligible in comparison with the inevitable errors of observation. Air thermometers consequently agree, not only when they are filled with air at the same pressure, but also when they are filled under considerably different pressures.

Regnault also operated with thermometers filled with other gases than air, such as hydrogen, carbonic acid, and sulphurous acid gas, determining the numerical coefficient for each by the mean expansion between 0° C. and 100° C. The instruments filled with the permanent gases agreed perfectly, or did not differ by more than 0°·1 or 0°·2 up to 340° C.

The sulphurous acid thermometer, however, did not show the same agreement, but differed from the normal air thermometer more and more with increase of temperature, the difference amounting to nearly 3° C. at 300° C.

The influence of the quality of the glass in the bulb was also considered, and it was found that the inequalities of expansion of different kinds of glass did not affect the readings of the thermometers by more than 0°·5 C. even at a temperature of 350°, and were consequently negligible as compared with other errors of experiment. This in itself is a strong argument in favour of the employment of a permanent gas as the standard thermometric substance.

Regnault also compared the normal air thermometer with mercury thermometers, the stems of which were graduated into divisions of equal volume, and also with overflowing (or weight) thermometers. With these thermometers, the absolute expansion of the liquid being small compared with that of air, the inequalities of expansion of the glass largely influence their indications, so that two mercury thermometers constructed with different kinds of glass, or even with the same kind of glass which has suffered different treatment before the blowpipe in the manufacture of the instrument, and which agree at 0° and 100°, will generally disagree at all other points of the scale. Dulong and Petit were under the impression that when one mercury thermometer is compared with the air thermometer, and a table of corrections drawn up, this same table of corrections might be applied to every other mercury thermometer. In other words, they supposed that mercury thermometers agreed amongst themselves. That this is not the case is amply proved by the researches of Regnault, and M. Is. Pierre[1] has

[1] *Ann. de Chimie et de Physique*, 3e série, tom. v. p. 427, 1842.

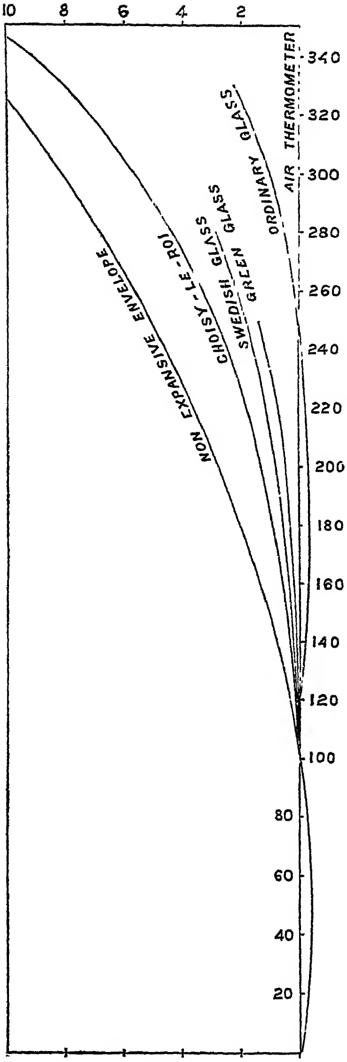


Fig. 22.

shown that two mercury thermometers constructed from the same piece of glass with the same care did not agree exactly[1] even between 0° and 100° C.

The annexed diagram taken from Regnault's work shows the relation of mercury thermometers constructed with different kinds of glass to the normal air thermometer, and also to a thermometer depending on the absolute expansion of mercury, that is one with a non-expanding bulb. It shows that the dilatation of mercury apparent and real increases with the temperature registered by the air thermometer, that mercury in ordinary soft glass keeps much nearer to the air thermometer than mercury in hard Choisy-le-Roi crystal, and this also closer than an independent mercury thermometer. Hence there is shown an augmentation in the expansion of all kinds of glass with temperature, and this more so in the case of ordinary soft glass than in hard Choisy-le-Roi, the expansion of the former being nearly sufficient to correct for the increased expansion of the mercury.

Between 0° and 100° the independent mercury thermometer stands lower than the air thermometer, and about 50° this difference is as much as 0·35° C. The curves for the other thermometers are not shown

[1] Since the time of Dulong and Petit many experiments have been made on the comparison of air and mercury thermometers, but unfortunately most of them have been executed only at high temperature. All experiments have shown that between 0° C. and 100° C. the mercurial stands above the air thermometer. No general rule for all kinds of glass can be laid down. Rowland proposes the formula

$$\theta' = \theta + a\theta\,(100 - \theta)\,(b - \theta),$$

in which θ' is the temperature centigrade by mercury thermometer, and θ the corresponding temperature on the air thermometer.

between 0° and 100°, but for Choisy-le-Roi glass the indication will be lower than that of the air thermometer by about 0°·2 C. at 50° C., and the ordinary soft glass thermometer will stand above the air thermometer between 0° and 100° by about 0°·2, or 0°·3 at 50° C. This inference follows from Regnault's tables, which are appended.

Air Ther.	Choisy-le-Roi.	Ordinary Glass.	Green Glass.	Swedish Glass.
100	100·00	100·00	100·00	100·00
110	110·05	109·98	110·03	110·02
120	120·12	119·95	120·08	120·04
130	130·20	129·91	130·14	130·07
140	140·29	139·85	140·21	140·11
150	150·40	149·80	150·30	150·15
160	160·52	159·74	160·40	160·20
170	170·65	169·68	170·50	170·26
180	180·80	179·63	180·60	180·33
190	191·01	189·65	190·70	190·41
200	201·25	199·70	200·80	200·50
210	211·53	209·75	211·00	210·61
220	221·82	219·80	221·20	220·75
230	232·16	229·85	231·42	230·90
240	242·55	239·90	241·60	241·16
250	253·00	250·05	251·85	251·44
260	263·44	260·20	262·15	...
270	273·90	270·38	272·50	...
280	284·48	280·52	282·85	...
290	295·10	290·80	293·30	...
300	305·72	301·08	...	...
310	316·45	311·45	..	...
320	327·25	321·80	...	..
330	338·22	332·40	...	...
340	349·30	343·00	..	...
350	360·50	354·00	...	...

M. Bertholet[1] has examined the results of some experiments of M. Violle, and has concluded that two air thermometers, one defined by equal increments of pressure at constant volume, and the other by equal increments of heat, agree between 0° C. and 200° C., but disagree at higher temperatures more and more till, when the first indicated 4500°, the second marked 8815°. He surmises that this points to a breaking up of the groups of molecules at high temperature, or of dissociation of the molecules themselves.

The following table shows the deviations of an ordinary alcohol thermometer from the standard air thermometer, after Jolly.[2] A similar comparison has been since made by Mr. A. C. White,[3] with substantially the same results.

[1] *Ann. de Chimie et de Physique*, vol. iv. pp. 84, 90, 1885.

[2] Jolly, *Pogg. Ann. Jubelband*, 1874.

[3] A. C. White, *Proc. American Academy of Arts and Sciences*, vol. xxi. pt. i. p. 45, 1885.

Air Thermometer.	Alcohol.	Difference.
$-6°\cdot32$	$-6°\cdot21$	0·11
$-11\ \cdot02$	$-10\ \cdot72$	0·30
$-15\ \cdot25$	$-14\ \cdot41$	0·84
$-19\ \cdot29$	$-18\ \cdot02$	1·27
$-79\ \cdot44$	$-70\ \cdot72$	8·72

Exercises

1. If the thermometric substance obeys Boyle's law, and if changes of temperature be taken proportional to changes of pressure at constant volume, show that the characteristic equation of the substance is $pv=R\Theta$.

[As in Art. 82 we have $\theta-\theta_0=(p-p_0)\phi(v)$, or

$$\Theta=p\phi(v),$$

the zero of temperature being that at which the pressure is zero, and the right-hand member of the equation is the function of p and v, which remains constant at constant temperature, namely pv, therefore $\phi(v)$ is proportional to v, etc.]

2. Find the characteristic equation of a substance which, when used as a thermometric substance, will give the same scale of temperature, whether it is designed to measure equal changes of temperature by equal changes of volume under constant pressure, or by equal changes of pressure at constant volume.

[In the former case we have, as before, the temperature proportional to the volume, or

$$\Theta=vf(p);$$

and in the second method we have

$$\Theta=p\phi(v).$$

Hence if Θ is to be the same in both cases we must have

$$vf(p)=p\phi(v),$$

or

$$\frac{f(p)}{\phi(v)}=\frac{p}{v}.$$

That is, $f(p)$ is proportional to p and $\phi(v)$ to v, and therefore the substance obeys Boyle's law.]

3. If ρ_1 and ρ_2 be the densities of two gases under the same pressure and at the same temperature, show that

$$\rho_1R_1=\rho_2R_2.$$

[Let v be the volume of unit mass of a gas of density ρ, then $\rho v=1$, so that the equation $pv=R\Theta$ becomes

$$\frac{p}{\rho}=R\Theta,\ \text{or}\ \rho R=\frac{p}{\Theta}.$$

Hence if different gases are at the same temperature and pressure, we have

$$\rho_1R_1=\rho_2R_2=\text{etc.}=\frac{p}{\Theta}.$$

For air $\rho=0\cdot001293$ when $p=760$ cm. of mercury$=1033\cdot3$ grammes per square centimetre. Therefore

$$R=\frac{1033\cdot3}{0\cdot001293\times273}=2927.$$

For any other gas the value of R will be found by means of the relation established above, that is by dividing the value of R for air by the relative density of the gas. The density of nitrogen relative to air is 0·97137, and the value of R is 3013. For oxygen the relative density is 1·10563, and the value of R is 2647. For hydrogen the relative density is 0·06926, and the value of R is 42261.]

4. If the different parts of a gas, having volumes v_1, v_2, v_3, etc., be at temperatures Θ_1, Θ_2, Θ_3, etc., and if in any other condition the same parts have volumes v_1', v_2', v_3', at temperatures Θ_1', Θ_2', Θ_3', etc., show that

$$\Sigma\frac{p_1v_1}{\Theta_1}=\Sigma\frac{p_1'v_1'}{\Theta_1'}.$$

[The mass of the whole volume is $\Sigma\rho_1v_1$ and also $\Sigma\rho_1'v_1'$, where ρ_1 is the density of the volume v_1 under the pressure p_1 and at the temperature Θ_1, and ρ_1' the density under p_1' and Θ_1'. Hence we have

$$\Sigma\rho_1v_1=\Sigma\rho_1'v_1'.$$

But

$$\rho_1=\frac{\rho_0 p_1}{p_0}\frac{\Theta_0}{\Theta_1}, \text{ etc.}$$

Therefore by substitution we have

$$\Sigma\frac{p_1v_1}{\Theta_1}=\Sigma\frac{p_1'v_1'}{\Theta_1'}.]$$

5. If a gas departs from Boyle's law, show how to calculate the temperatures of a constant volume air thermometer from observations on a constant pressure instrument.

SECTION III

PYROMETRY

87. Measurement of High Temperatures.—Instruments designed for the measurement of high temperatures are called pyrometers. The accurate estimation of elevated temperatures is a task of no ordinary difficulty, and for this purpose the variation of almost every physical property of matter with temperature has been proposed.

The range of every thermometer is limited by the nature of the materials with which they are constructed. Thus at high temperatures liquids boil, and at low temperatures they freeze, and even if this did not occur, an upper limit to the range of any liquid or gas thermometer is presented at the fusing point of the material of which the envelope is constructed.

The ultimate practical standard of reference in pyrometry is the air thermometer furnished with a porcelain bulb. The method of measuring temperature by the change of volume or pressure of a gas having been once chosen, all other instruments for measuring temperature must be standardised either by direct or indirect comparison with the air thermometer, if their indications are to have any intelligible meaning.

The pyrometer of Deville and Troost[1] is a modified form of air thermometer furnished with a porcelain bulb. A glass bulb cannot be used for high temperatures on account of the fusion of the glass, and platinum bulbs were found by Deville and Troost to be permeable to gases at high temperatures. The porcelain bulb is filled with dry air and placed in the furnace, and when equilibrium of temperature is attained the stem is sealed by an oxyhydrogen flame. The apparatus is then allowed to cool and the end of the stem is nipped off under mercury, so that the mercury rises into the bulb. The bulb is then depressed until the mercury stands at the same level within

[1] Deville and Troost, *Ann. de Chimie et de Physique*, 3e série, tom. lviii. p. 257, 1860.

and without. The stem is now closed with wax, and the apparatus removed and weighed, with the mercury it contains. It is afterwards completely filled with mercury and weighed again. By this means the fraction of the gas which escapes by expansion while in the furnace is determined, and consequently the whole expansion under constant pressure is known, and the temperature of the furnace determined.

The pressure of the residual air instead of its volume may be determined when it has cooled. For this purpose the bulb is provided with a long fine neck and a tap, which communicates with a manometer. This tap is left open while the bulb is in the furnace, and is osed when the final temperature is reached. The bulb is then allowe._ to cool, and the residual pressure determined by connecting it with the manometer.

To complete the accuracy of this instrument, it is necessary to know the coefficient of expansion of porcelain, and any uncertainty in the value of this coefficient will limit the accuracy of the indications of the instrument. All uncertainty from this cause disappears in a vapour-pressure thermometer in which it is the pressure alone that is to be measured, and not the volume or the pressure under any given volume.

We shall now consider some of the various methods which have been proposed for the estimation of high temperatures.

88. The Method of Cooling.—One of the earliest attempts at pyrometry was that of Newton,[1] in the estimation of the temperature of red-hot iron. The method employed consisted in observing the time required by the heated mass to cool under given conditions. Assuming a certain law of cooling to hold at all temperatures, then by observing the rate of cooling at known temperatures, the data necessary to estimate the initial temperature may be obtained from the time of cooling to some other known temperature. The law assumed by Newton was that the rate of cooling of a body under given conditions is proportional to the temperature difference between the body and its surroundings, and this law has since passed under the name of Newton's law of cooling.

If such a law were found to hold accurately at all temperatures within the range of our standard thermometer, then such an agreement might warrant the use of the law and methods founded on it to extend the scale of temperatures beyond the limits of the standard thermometer. No such agreement has, however, been found, and it is only for very moderate differences of temperature that the law appears to be even approximately verified. In this case, then, the application

[1] Newton, "Scala Graduum Caloris," *Phil. Trans.* vol. xxii. p. 824, 1701.

of the method to the measurement of temperatures beyond the range of standard instruments would be illegitimate and unreasonable.

89. Pyrometry by Vapour Densities.—The direct observation of the density of mercury vapour was suggested by Regnault[1] as a method of estimating high temperatures. Some mercury is placed in a wrought-iron flask and exposed to the temperature to be measured. As the mercury boils away the air is expelled, and the flask is finally left filled with the vapour of mercury at the temperature of the furnace. When temperature equilibrium is attained the mouth of the flask is covered with a lid, so that the neck is closed and the flask is allowed to cool. The vapour condenses, and the liquid mercury is collected and weighed. Assuming the vapour to obey the laws of a perfect gas, the temperature may be easily calculated from the known density of mercury vapour and the volume of the flask corrected for expansion. A porcelain flask furnished with a ball stopper may be used instead of one of wrought iron.

The vapour of iodine has been used by Deville and Troost for the same purpose. The iodine was enclosed in a porcelain flask of about 300 c.c. capacity, furnished with a fine stem, which just protruded from the furnace chamber. The nozzle was closed by a loosely fitting stopper, past which the vapour could escape. When the iodine was completely vaporised and equilibrium of temperature established, the stopper was fused into the nozzle by an oxyhydrogen blowpipe. The weight of the iodine still remaining in the flask was determined as soon as it cooled, and the volume of the flask and the density of iodine vapour being known, the temperature of the furnace was estimated. The correction for the expansion of the flask was made by noting the elongation of a rod of porcelain for temperatures up to 1500° C.

90. Siemens's Pyrometer.—The electric resistance of a metallic wire is found to increase gradually with the temperature, and consequently on this property a system of thermometry may be established. The pyrometer invented by Siemens[2] depends on the change of the electric resistance of a platinum wire when heated. The wire (Fig. 23) was doubled and wound on a cylinder of refractory fireclay. When thus coiled its ends were fastened to stout platinum wires of such a length that their further ends are never very warm, and these in turn were connected by copper wires to the binding screws on the outside of the case of the pyrometer. The copper wires were enclosed

[1] Regnault, *Ann. de Chimie et de Physique*, 3^{e}, tom. lxiii. p. 39, 1861.

[2] C. Wm. Siemens, *Phil. Mag.* vol. xlii. p. 150, 1871 ; see also *Brit. Ass. Report*, 1874.

in a stout wrought-iron tube of about 3·5 cm. diameter and 120 cm. in length which projected from the furnace or other space whose temperature was to be measured, and formed a handle of support for the whole instrument. The platinum coil was enclosed in a sheath, of platinum, or wrought iron, fastened to one end of the iron tube, and the coil was packed in this sheath with asbestos to prevent shifting.

The most important point to determine is the constancy of the resistance of the coil at a given temperature, or if it will always be

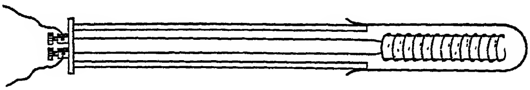


Fig. 23.

the same at the same temperature. A thermometer should be free from secular changes of its zero, and it should therefore be determined how much, if any, permanent alteration occurs in the resistance of the platinum wire after prolonged or repeated exposure to high temperatures. These points were examined by a committee of the British Association.[1] Denoting the resistance of the coil at 10° C. by R_{10}, and its resistance at $\theta°$ by R_θ, the formula employed was [2]

$$R_\theta = R_{10}[1 + a(\theta - 10)],$$

where a is a constant depending on the nature of the wire.

[1] See *Brit. Ass. Report* for 1874.

[2] The problem of the variation of electrical resistance with temperature was first attacked by Sir Wm. Siemens. He proved that the formula given by Matthiessen

$$R_0 = R(1 - \alpha\theta + \beta\theta^2),$$

where R is the resistance at θ and R_0 the resistance at zero, was quite inapplicable except between the limits 0° and 100° C. His own experiments led him to suggest the formula

$$R = \alpha\Theta^{\frac{1}{2}} + \beta\Theta + \gamma,$$

but the more recent experiments of Callendar have proved that this formula does not represent the results of observation so well as a simple formula of the ordinary type,

$$R = R_0(1 + \alpha\theta + \beta\theta^2).$$

The formula in the text is a particular case of this in which 10° C. is taken instead of the zero.

Siemens's experiments were published in the *Transactions of the Society of Telegraph Engineers*, 1875. They were of a very rough character, and were undertaken merely with the object of graduating a commercial pyrometer.

Siemens applied the variation of the resistance of platinum to the measurement of deep-sea temperatures. Two coils of platinum wire of equal resistance were employed. One of these was let down to the sea bottom, and the other was placed in a bath, the temperature of which was varied till equality of resistance was restored between the coils. The temperature of the sea bottom was then the same as that of the bath.

In the case of coils surrounded by a platinum sheath exposure to high temperatures caused no serious permanent change in the resistance, but a considerable permanent increase of resistance was caused in those coils which were enclosed in iron sheaths. These alterations were due to prolonged exposure to high temperatures rather than to alterations from high to low, and as Professor Williamson pointed out arose from a permanent alteration of the platinum coil caused by the combined action of the atmosphere inside the iron case, and the silica of the fireclay cylinder on which the coil is wound. Such permanent alterations of the resistance of the spiral of course destroy the accuracy of the instrument, and it is obvious that the fireclay cylinder should be replaced by something less objectionable, or dispensed with altogether. With this view the thorough examination of the properties of the instrument, and of its qualifications as a reliable standard of reference, was undertaken by Mr. H. L. Callendar [1] with such favourable results, that he considers the platinum resistance thermometer not only a trustworthy instrument in pyrometry, but also that it possesses those permanent qualities which recommended it specially as a standard of reference in thermometry.

91. Platinum Resistance Thermometers.—After a careful investigation of the variations of the resistance of platinum wire with temperature, Mr. Callendar concluded that pure platinum wire, free from alloy with silicon, carbon, tin, or other impurities, when not subjected to strain or rough usage, possessed always the same resistance at the same temperature. Different lengths of the pure wire were found to behave similarly, and their resistances were not found to be subject to any permanent change from heating and cooling, provided they were not strained or chemically altered. It therefore possesses in a high degree the qualifications necessary to a scientific standard. Thus while the air thermometer possesses several advantages as an ultimate standard it is practically impossible to use it in ordinary work, while the platinum thermometer, on the other hand, when once standardised by comparison with the air thermometer, can be readily used, and may be subsequently employed as a standard of comparison for other thermometers, and thus the elaborate precautions and special apparatus otherwise necessary for this purpose are avoided. The practical difficulty in the comparison of thermometers is the maintaining of an enclosure at a constant temperature, but in the standardising of the platinum thermometer this difficulty is avoided by enclosing the spiral in the bulb of the air thermometer.

Assuming the simple formula $R = R_0(1 + \alpha\theta_p)$, it follows that the

[1] H. L. Callendar, *Phil. Trans.*, 1887, p. 161.

temperature θ_p, registered by the platinum thermometer when its resistance is R, will be

$$\theta_p = 100 \frac{R - R_0}{R_{100} - R_0}.$$

This will differ somewhat from the temperature θ registered by the air thermometer, because the assumed formula for R is not applicable through any extended range, but Callendar found that the difference of the indications of the two instruments may be represented through a very wide range with great accuracy by the parabolic formula

$$\theta - \theta_p = \delta \left\{ \left(\frac{\theta}{100}\right)^2 - \frac{\theta}{100} \right\},$$

where δ is a constant to be determined for the particular specimen of wire employed, and may be obtained from a single observation of the boiling point of sulphur[1] or mercury, or some other substance, whose boiling point θ is accurately known. The first work of Callendar was soon afterwards confirmed by Mr. E. H. Griffiths,[2] who found that the above formula possessed greater accuracy than even Callendar supposed.[3]

In the form adopted by Mr. Griffiths the platinum wire was wound on a roll of asbestos paper, its ends being soldered to thick copper leads (communicating with binding screws), which for the sake of insulation were enclosed in narrow glass tubes.

The great superiority of the platinum resistance thermometer over liquid-in-glass thermometers lies not only in its far wider range, but also in its comparative freedom from changes of zero. The wire when pure and well annealed has always sensibly the same resistance at the same temperature. Thus while it is difficult to attain an accuracy of $\frac{1}{10}$th of a degree at temperatures as low as 200° C. with a mercury thermometer, with a properly constructed platinum thermometer the zero does not vary by $\frac{1}{100}$th of a degree at any temperature up to 500° C., and in some of Callendar's thermometers it was found not to change more than $\frac{1}{10}$th of a degree up to 1300° C. For temperatures below 700° C. the coil and leads may be enclosed in a tube of dimensions similar to those of an ordinary thermometer, and the leads may be of copper or silver and the tube of hard glass. For accurate work at high temperatures platinum leads must be used, and the whole must be enclosed in a tube of glazed porcelain. For in-

[1] See Callendar and Griffiths, *Phil. Trans.*, A., p. 161, 1887.

[2] E. H. Griffiths, *Proc. Roy. Soc.*, December 1890.

[3] For this reason it has been also proposed by T. Ewan and W. W. Haldane Gee to issue these thermometers as standards of comparison for liquid thermometers (*Proc. Manchester Lit. and Phil. Soc.*, 1890-91, p. 357).

sulating the coil and leads nothing answers so well as mica.[1] Most varieties of clay are apt to attack the wire at high temperatures, and the large mass of a clay cylinder reduces the delicacy of the instrument. The wire is preferably doubled on itself like an ordinary resistance coil and then wound on a thin plate of mica (Fig. 24), the leads being insulated by being made to pass through a series of mica wads cut to fit the tube containing the instrument. This gives very perfect insulation, and prevents convection currents of air up and down the tube.

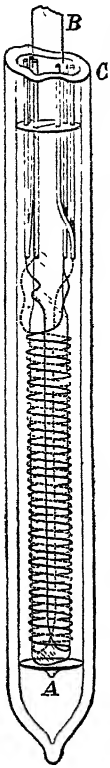


Fig. 24.

When measurements are made with an ordinary post-office resistance box, results may be obtained which are consistent to a few hundredths of a degree up to 500° C., provided the resistance of the leads is small and fairly constant. Very thick leads, however, are objectionable, not only from their want of lightness and flexibility, but also from their cooling action on the spiral by conduction along the stem. For most purposes it is therefore better to use light leads, and to insert in the stem a second pair of leads similar to the first, so that their resistance can be measured separately and allowed for at any temperature. By this means leads of any convenient length and flexibility may be employed, and the observations will be independent of the length of stem immersed.

With a mercury thermometer, on the other hand, some portion of the stem must be exposed to the air, and the correction arising in this respect is so uncertain that it is now generally avoided by using a series of thermometers of "limited scale." Each of these must have at least two points of its scale specially determined. This has been hitherto done by means of substances of known boiling points and freezing points, but, as Griffiths has shown,[2] the graduation may be more easily and accurately effected by comparison with a single platinum thermometer. Thus a single platinum thermometer may be used to do the work of a whole series of liquid-in-glass thermometers with far greater accuracy and without the necessity of applying any troublesome and uncertain corrections.[3]

The method recommended by Callendar and Griffiths for standardising the platinum thermometer is by the observation of the boiling

[1] H. L. Callendar, *Phil. Mag.*, July 1891, p. 104.

[2] E. H. Griffiths, *Brit. Ass. Report*, 1890.

[3] Callendar and Griffiths, *Phil. Trans.*, 1891, A., pp. 119-157.

point of sulphur, on the supposition that the temperature of the vapour of sulphur boiling under 760 mm. pressure is $444°\cdot53$ C. on the air thermometer, allowing $0°\cdot082$ C. for each mm. of pressure different from this. This temperature of boiling sulphur was obtained previously from a series of very careful experiments.[1] Method of standardising.

Thus when R_0 and R_{100} have been determined as well as R for some third known temperature (the boiling point of sulphur), then θ_p for this temperature becomes completely determined, and by substituting in the formula for $\theta - \theta_p$ the value of δ is deduced. The determination of the resistance in boiling sulphur is attended with difficulties, and requires a special apparatus, but it has been recently shown by Griffiths and Clark[2] that this determination may be avoided by assuming, in accordance with the observations of Dewar and Fleming, that the resistance of certain pure metals (including platinum) diminishes at low temperatures in such a way as to lead to the conclusion that at absolute zero it vanishes. This gives $R = 0$ when $\theta = -273$, and consequently when a high order of accuracy is not a *sine qua non*, and when the spiral is known to be tolerably pure, this value may be used with R_0 and R_{100} to determine δ, and the instrument can be graduated by direct observations of R in steam and melting ice alone.

Another form of resistance thermometer is that described by Mr. W. N. Shaw.[3] In this instrument one arm of a Wheatstone's quadrilateral is a platinum wire and the other three consist of platinum-silver wire. The platinum wire and the alloy have different temperature coefficients, and consequently, if the arms of the quadrilateral are so arranged that a balance exists at any definite temperature, then at all other temperatures equilibrium will be destroyed, but the balance may be restored by shunting the platinum arm. This can be effected by connecting a resistance box in a suitable manner with the projecting leads, and the resistance of the shunt required to produce a balance may be employed to indicate the temperature when the instrument has been graduated. The wires of the quadrilateral are laid side by side and enclosed between two strips of india-rubber, so as to take the form of a narrow flexible ribbon which can be rolled round a cylinder or burette, the mean temperature of which is required. The graduation was effected by winding the ribbon on a metal cylinder, and immersing the whole Shaw's Bridge.

[1] An interesting series of experiments with this instrument on the melting point of silver has been described by Mr. Callendar in the *Philosophical Magazine*, Feb. 1892, p. 220.

[2] E. H. Griffiths, and G. M. Clark, *Phil. Mag.* vol. xxxiv. p. 515, Dec. 1892.

[3] W. N. Shaw, *Brit. Ass. Report*, Bath, p. 590, 1888.

in ice or a water bath, and taking readings at various temperatures. With a suitable galvanometer a variation of about $\frac{1}{500}$ of a degree of temperature may be detected.[1]

92. Other Methods.—Various other effects of heat have been suggested, and used, as the basis of systems of measuring temperature. Instruments constructed on any such basis must, however, be graduated by direct or indirect comparison with the air thermometer or other standard instrument, in order to give any intelligible numerical results. When once standardised, so as to agree with the air thermometer throughout its whole range, they may be used by extrapolation to register temperatures beyond that range, it being assumed that the instrument behaves beyond the range in the same manner as within it.

By calorimetry.

Such, for example, is the method of determining the melting point of platinum by calorimetry. This method is convenient, and often employed to determine the temperatures of furnaces. For this purpose the mean specific heat of some metal, such as copper, platinum, or wrought iron, must be determined in advance. A portion of the chosen metal is then heated in the furnace, and when it has attained the temperature of the latter it is removed and placed in a calorimeter. The quantity of heat it gives out in cooling in this instrument is measured, as explained in chapter iv., and from this experiment the temperature of the mass of metal when placed in the calorimeter can be computed. This method is subject to a serious error in the loss of heat which inevitably accompanies the transference of the metal from the furnace to the calorimeter, besides suffering from all the errors which attend such a difficult experiment as the determination of a quantity of heat by means of a calorimeter.

By elongation.

The measurement of high temperatures by the elongation of a bar of metal has been frequently employed. The first pyrometer of this kind is attributed to Muschenbrock, and others were devised in the early part of this century by Des Aguliers, Ellicot, Graham, Smeaton, Ferguson, Brogniart, Laplace and Lavoisier, and later by Pouillet.[2] This method can be employed with accuracy only if the expansion is referred to a scale kept at a fixed temperature, as explained in Art. 98, and in this respect Pouillet's pyrometer is superior to those previously employed. In Daniell's pyrometer the relative expansion of a metal bar in an earthenware socket was used, and more recently Steinle and Harting[3] employed the expansion of graphite. Weinhold,[4] however,

[1] For an account of Joly's meldometer, a beautiful apparatus for determining the melting points of crystals, see the *Proceedings of the Royal Irish Academy*, 3rd Series, vol. ii. p. 38, 1891.

[2] See Art. "Pyrometry," *Ency. Brit.*

[3] Beckert, *Zeitschr. f. Anal. Chem.* vol. xxi., A., p. 284, 1882.

[4] Weinhold, *Pogg. Ann.* vol. cxlix. p. 186, etc., 1873.

after investigating this class of instruments, states that it is not possible to obtain trustworthy results by the relative expansion of solids. Wedgewood's pyrometer[1] depended on the contraction of a short cylinder of fine fireclay when exposed to a high temperature, and then allowed to cool. Such an instrument, of course, could only give a very rough idea of the temperature of a furnace.

The measurement of high temperatures by the electromotive force of a thermo-electric couple has been tried repeatedly. A platinum-iron couple was employed by Rosetti[2] to measure the temperatures of flames, and a platinum-palladium couple by E. Becquerel.[3] Sufficient knowledge of the behaviour of such couples at high temperatures does not appear to be at hand to establish confidence in the constancy or accuracy of their indications. The most elaborate and accurate experiments on the subject are those of Professor P. G. Tait.[4] Recently M. H. Le Chatelier[5] states that temperatures up to 1200° C. may be measured to within 10° by means of a thermo-electric couple. By electromotive force.

The variation of the wave length of sound has also been suggested as a means of measuring the density of air, and hence determining its temperature. The process would, however, be subject to such difficulties and sources of error that it must be regarded rather as a theoretical than a practical method in pyrometry.

93. Strain Thermometers.—Temperature may also be indicated by the strain, or change of shape of a heterogeneous substance through inequalities of expansion of its constituents. On this principle depend several forms of pocket thermometers and self-registering thermometers. Bréguet's metallic thermometer (Fig. 25) is a good example. In this instrument three thin strips of platinum, gold, and silver are fastened together (by being passed through a rolling mill) so as to form a thin ribbon, the core of which is gold and the surface layers platinum and silver respectively. This ribbon is then coiled into a spiral, one end of which is held fixed while the other carries a pointer moving round a graduated scale. The silver, which is most expansible, forms the inner face of the spiral; and the platinum, which is least expansible, the outer face. When the temperature rises the silver expands more than the gold or platinum, and the spiral unwinds itself, moving the pointer round the scale, the contrary effect being produced when the temperature falls. The instrument may be made a meter by graduating it by direct comparison with a standard thermometer, and if a Bréguet's.

[1] Described in *Phil. Trans.*, 1782, pp. 84, 86.
[2] Rosetti, *Ann. de Chimie et de Phys.*, 5e, tom. xvii. p. 177, 1879.
[3] E. Becquerel, *Ann. de Chimie et de Phys.*, vol. lxviii. p. 49, 3e, 1863.
[4] Tait, *Edin. Phil. Trans.* vol. xxvii.
[5] H. Le Chatelier, *Journal de Physique*, 2e, tom. vi. p. 23, 1887.

light index be placed on the scale so as to move before the pointer, it will give the maximum temperature during any period. A second index placed on the other side will give the minimum temperature. This thermometer is sensitive to very small changes of temperature.

Bourdon's. Another class of strain thermometer depends upon the change of shape of a thin flexible metal tube filled with a highly expansive liquid such as alcohol, chloroform, or a mixture of both (Fig. 26). The tube thus filled is sealed at a low temperature and bent into a circular arc. If now the temperature rises the volume of the contained liquid increases, and the tube straightens itself so as to increase its internal capacity. Hence if one end is fixed the other end will move with every variation of temperature, and if a pointer be attached to it the motion may be used to register temperatures. This method was due to

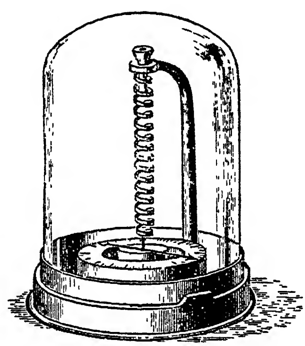


Fig. 25.

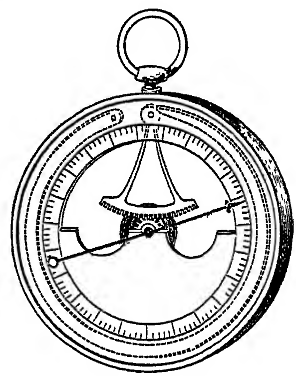


Fig. 26.

Bourdon, and it has since been adopted as a meteorological recording instrument, and also as a convenient form of pocket thermometer, which, when furnished with a maximum index, may be used as a clinical thermometer.

94. Joule's Air-Temperature Thermometer. — A thermometer indicates its own temperature, and for this reason it is difficult to determine the exact temperature of the air at any place, for the indications of a thermometer placed there will be influenced by the radiation of neighbouring bodies. To avoid this disturbing influence Joule[1] invented an apparatus depending on the motion (caused by an air current) of a spiral of fine wire suspended by a filament of silk, and carrying a small mirror which reflects a beam of light to a distant scale. The spiral wire is contained in a copper tube (Fig. 27) surrounded by another coaxal cylinder, and the space between the two is

[1] Joule, *Proc. Manchester Lit. and Phil. Soc.*, vol. vii. p. 35.

filled with water, the temperature of which is noted by means of a thermometer. The lower end of the tube containing the spiral is furnished with a lid which can slide backwards or forwards, so as to open or shut the aperture at pleasure. When the tube is closed the air within it comes to the temperature of the water, and if the lid be now removed, an upward current will set through the tube if the air within is warmer than that outside, and a downward current will set in if the reverse is the case. In case of equality there will be no current and no deflection of the mirror, or spot of light on the scale. Joule found that a difference of 1° F. produced an entire twist of the filament, and that the temperature of the water when equilibrium was secured was generally higher than that indicated by a thermometer exposed in the air outside.

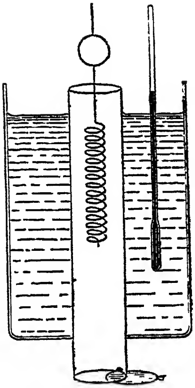


Fig. 27.—Joule's.

[For radiometers and sensitive thermometers see Chap. VI. p. 489.]

CHAPTER III

DILATATION

SECTION I

DILATATION OF SOLIDS

95. Cubical Expansion.—In approaching the subject of expansion by heat it is necessary to bear distinctly in mind the exact meaning, and mode of measurement, of temperature. It being agreed to measure changes of temperature by changes of the volume of some substance, under given conditions of pressure (hydrogen for example under constant pressure), we have then by definition a distinct relation between the volume and temperature of this substance, of the form

$$V = V_0(1 + \alpha\theta).$$

In this formula V_0 is the volume at the chosen zero of temperature, and equal changes of temperature are measured by equal changes of volume of this substance. The change of volume for one degree of temperature is αV_0, and α is a constant throughout the whole scale.

For other substances we might still retain a formula of the same shape in which α must be replaced by a function of the temperature, and the general expression for the volume at any temperature θ will be of the form

$$V = V_0(1 + a\theta + b\theta^2 + c\theta^3 + \ldots) = V_0(1 + \alpha\theta),$$

where

$$\alpha = a + b\theta + c\theta^2 + \text{etc.}$$

For most substances the coefficients b, c, etc., diminish very rapidly and the equation $V = V_0(1 + \alpha\theta)$ holds very approximately when α is regarded as a constant for each particular substance.

In the foregoing equations it is tacitly assumed that the volume of any substance under constant pressure is always the same at the same temperature, that is, that the volume, under given conditions of pressure, is a function of the temperature. This assumption will be legitimate if the volume depends only on the temperature and pressure, and this appears to be the case. Apparent exceptions occur in such substances as glass, in which the previous treatment

becomes a factor of importance and modifies the characteristics of the substance. The volume in such cases is not always the same at the same temperature, but it is to be observed that here we are not sure that the conditions of pressure are the same throughout the mass. In fact the well-known case of Rupert's drops indicates that glass which has been suddenly cooled is subject to intense internal stress, and the recovery from such stress is a very slow process. The process of "annealing" has been specially devised to obviate such abnormal conditions in solids. In the case of fluids there is, however, apparently no reason why the volume should not always be the same at the same temperature and under the same external pressure.

The mean coefficient of expansion between any two temperatures has already been defined as the mean increase in bulk of a unit volume per degree of temperature or

$$\frac{V'-V}{V(\theta'-\theta)}.$$

If the difference of temperature $\theta'-\theta$ be taken very small, the change of volume $V'-V$ will also be very small, and denoting these by $d\theta$ and dV respectively, the coefficient becomes

$$\frac{1}{V}\frac{dV}{d\theta} \quad . \; . \; . \text{ (true coefficient).}$$

This expression may be termed the *true* coefficient of expansion at the temperature θ.

Another coefficient is sometimes used which may be termed the *zero* coefficient of expansion. In this the zero volume V_0 replaces V as indicated by the expression

$$\frac{1}{V_0}\frac{dV}{d\theta} \quad . \; . \; . \text{ (zero coefficient).}$$

In the case of the thermometric substance, it is this zero coefficient of expansion that appears in the equation

$$V=V_0(1+a\theta),$$

and in this case a is absolutely constant, whereas the true coefficient will be aV_0/V, and this varies inversely as V.

COR. If the true coefficient of expansion be a constant a, the relation between volume and temperature is

$$\frac{dV}{V}=ad\theta,$$

or

$$V=V_0e^{a\theta}.$$

96. Apparent Expansion.—In the case of fluids contained in a solid envelope which acts as a measuring flask, we have another coefficient termed the coefficient of *apparent* expansion. In this case the rise or fall of the surface of the fluid in the neck of the flask indicates the apparent change of volume of the fluid.

Let V_a be the apparent volume of the fluid at the temperature θ, and let V_0 be its real volume at zero. Thus the flask may be standardised and graduated at zero so that the volume indicated at this temperature is the real volume of the fluid. In this case the coefficient of apparent expansion is defined by the equation

$$V_a = V_0(1+a\theta) \quad . \quad . \quad . \quad (1).$$

The relation between the coefficient a and the real expansion of the fluid may be easily determined. For the real volume of the fluid is

$$V = V_0(1+\alpha\theta) \quad . \quad . \quad . \quad (2),$$

and if g denotes the coefficient of cubical dilatation of glass (or the material of the flask) we have also

$$V = V_a(1+g\theta) \quad . \quad . \quad . \quad (3),$$

since V_a is the internal capacity of this portion of the flask at zero. Hence equating (2) and (3) we have

$$V_0(1+\alpha\theta) = V_a(1+g\theta).$$

And using (1) we obtain

$$1+\alpha\theta = (1+a\theta)(1+g\theta),$$

or approximately, since all the coefficients are small,

$$\alpha = a + g.$$

97. Linear and Superficial Expansion.—In the case of bars the elongation or linear expansion also comes into consideration. In this case the coefficient of linear expansion is defined as before, as the elongation per unit length for one degree change of temperature. If l denotes the length of the bar at θ, and l_0 its length at zero, the true coefficient of linear expansion at θ will be

$$\frac{1}{l}\frac{dl}{d\theta},$$

and the zero coefficient will be

$$\frac{1}{l_0}\frac{dl}{d\theta}.$$

Denoting the latter by λ we have the general equation

$$l = l_0(1+\lambda\theta),$$

in which λ may be regarded as approximately constant. The rela-

tion connecting the linear and cubical dilatations is easily found. For the volume at θ of a cube whose side is l_0 at zero is $l_0^3(1+\lambda\theta)^3$ and the volume of the same cube is $V_0(1+\alpha\theta)$. But $l_0^3=V_0$, therefore

$$1+\alpha\theta=(1+\lambda\theta)^3,$$

or approximately

$$\alpha=3\lambda.$$

The coefficient of superficial expansion is defined in the same manner and may be shown to be twice the coefficient of linear expansion.

98. Determination of the Linear Expansion of Bars—Ramsden's Method.—The best mode of determining the coefficient of linear expansion of a substance is by the direct observation of the change of length of a bar of the material, the measurement of the length and change of length being referred to a scale kept at a fixed temperature. This method is applicable when bars of suitable length can be procured and was adopted by Ramsden to estimate the linear expansion of the bars used by General Roy[1] in his measurement of a base-line on Hounslow Heath.

The apparatus is shown in outline in Fig. 28, and consists essentially of three troughs fixed parallel to each other. The middle trough contains the bar to be experimented on, and can be heated by lamps placed underneath. The first and third troughs contain each an iron bar packed in broken ice so that they are kept constantly at a fixed temperature, and furnish a fixed length with which the length of the bar in the middle trough may be compared. In order to carry out this comparison the ends of the bars are furnished with adjustable uprights carrying lenses, eye-pieces, and cross wires. The first bar carries an eye-piece at each end supplied with a cross wire, and the middle bar is supplied at each end with a lens, so that each of these lenses acts as an object-glass to the corresponding eye-piece on the first bar. The lenses on the middle bar and the eye-pieces on the first thus constitute two telescopes, and these are adjusted so as to view two cross wires supported on the ends of the third bar and illuminated by mirrors situated behind. Since the first and third bars are kept in melting ice the eye-pieces and cross wires attached to them remain fixed, but when the temperature of the bar in the middle trough changes, the object-glasses attached to it will be displaced. In making an experiment the three troughs are filled with ice and the apparatus adjusted so that the images of the cross wires on the third bar are in exact coincidence with the cross wires of the eye-pieces, and matters are so arranged that the

[1] Roy, *Phil. Trans.*, 1785, p. 461.

middle bar is fixed at one end and free to move at the other so that when the temperature rises the lens at this end alone will move. If the other end should move during the experiment it can be easily detected and allowed for. Hot water is now placed in the middle trough and the temperature kept as stationary as possible by means of the lamps underneath. The bar in this trough expands and the object-glass on the free end is displaced by an amount $l - l_0$, where l is the length of the bar at the temperature θ of the bath and l_0 its length at zero. This displacement is measured by a very fine micrometer screw. By means of this screw the lens may be moved back into its original position so that the image of the distant cross wire is again superposed on the cross wire in the eye-piece. The

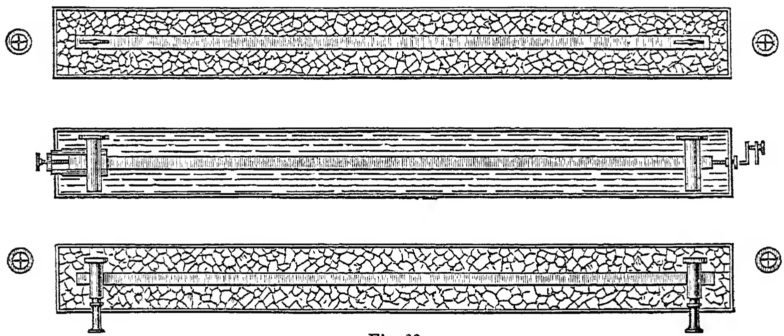


Fig. 28.

length $l - l_0$ being thus determined, the mean coefficient of expansion of the bar between 0° and θ° is

$$\lambda = \frac{l - l_0}{l_0 \theta}.$$

In Ramsden's apparatus the micrometer was not attached to the object-glass on the end of the middle bar, but to the eye-piece at the end of the first bar. Coincidence of the cross wires was then restored by moving the eye-piece. This displacement of the eye-piece was not the expansion $l - l_0$, but greater than this is the ratio of the distance between the first and third bars to the distance between the second and third. By attaching the micrometer to the object-glass on the middle bar the necessity for determining these distances is avoided.

The parallelism of the three bars is desirable, but excessive precaution in this respect is not absolutely necessary.

99. Method of Laplace and Lavoisier.—In the method devised by MM. Laplace and Lavoisier, the expansion $l - l_0$ is not directly measured, but is amplified into a much greater length by means of a

lever arrangement. The bar (Fig. 29), whose expansion is to be measured, is fixed at one end, but free to move at the other, which presses against the stiff arm of a lever. The other end of this arm carries a telescope directed towards a distant vertical scale. When the bar expands it pushes the arm before it, and turns the telescope round a horizontal axis, as shown (exaggerated) in figure.

If a be the length of the arm, and b the distance of the axis of rotation of the telescope from the fixed scale, and δ the observed displacement on this scale, we have at once

$$\frac{l-l_0}{a}=\frac{\delta}{b}.$$

Hence the mean coefficient of linear expansion is given by the equation

$$\lambda=\frac{a\delta}{bl_0\theta}.$$

In this method, although the distance δ may be very much larger than $l-l_0$, yet there are many sources of error attending the accurate

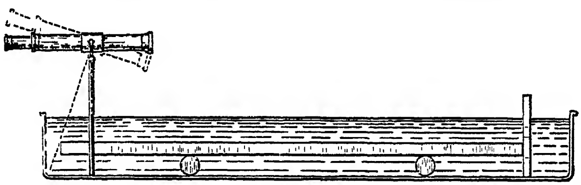


Fig. 29.

estimation of the quantity a, and any error in this gives rise to a proportional error in the value of λ.

100. Relative Expansion—Differential Method.—A differential method of observing the expansion of a bar, by comparison with another of known coefficient of expansion, was suggested by De Luc,[1] and adopted by Borda,[2] to determine the expansion of the bars used in the measurement of the French meridian degree.

Two bars, AB and A'B' (Fig. 30), are fastened together at one end, AA', and are free to slide on each other, during expansion, throughout their entire length, to their other ends. At their free ends, BB', they are graduated so that the two scales constitute a vernier which measures the relative expansion of the bars. The longer bar is made of platinum, and the shorter may be of any other metal which it is desired to compare with platinum.

A pair of bars arranged in this manner indicates their own temper-

[1] De Luc, *Journal de Physique de Delamétherie*, tom. xviii. p. 363, 1781.

[2] See Biot's *Traité de Physique*, tom. i. p. 164.

ature, for if the reading of the vernier be noted when the system is at 0° and 100°, or any other two known temperatures, the temperature of the apparatus may be deduced at any other time by means of the reading of the vernier alone.

When the coefficient of absolute expansion of the platinum bar is known, that of the other can be inferred, and, in this manner, Dulong and Petit determined the expansion of several solids.

Different specimens of the same metal vary considerably in their

FIG. 30.

physical properties, on account of impurities, or different mechanical actions to which they may have been subjected. For this reason, the coefficient of expansion obtained for any metal will depend on the specimen employed, and considerable discrepancies exist between the results obtained by different observers. Hence, if the expansion of any particular bar is required accurately, it must be determined by direct observation, for it cannot be assumed to be the same as that of any other specimen of the same material.

SECTION II

DILATATION OF LIQUIDS

101. Comparison of Densities.—In the case of fluids we have to deal with the cubical expansion only, and, as in the case of solids, the approximate formula,

$$V = V_0(1 + \alpha\theta),$$

may be employed, when α is regarded as a constant, namely, the coefficient of absolute expansion at zero.

In general, liquids are more highly expansive than solids, and it is for this reason that the level of the mercury rises in the stem of a thermometer when the instrument becomes warmer. Such an instrument is, therefore, well suited to the measurement of the relative or apparent expansion of a liquid, and, if the absolute expansion of the glass of the instrument be known, the absolute expansion of the liquid can be deduced by means of the formula of Art. 96. The linear expansion of glass may be found by the methods of the foregoing section, and from this the cubical expansion is deduced by means of the formula $\alpha = 3\lambda$. Having determined the cubical expansion of glass in this manner, Lavoisier[1] and Laplace deduced the coefficient of absolute expansion of mercury by a comparison of the mercury thermometer with a standard air thermometer between 0° and 100° C.

The weight thermometer (Art. 79) also gives the apparent expansion of the liquid with which it is filled, and, when the dilatation of the glass is known, the absolute expansion of the liquid is obtained. In this manner, Regnault deduced the absolute expansion of mercury by comparing the indications of an air and a weight thermometer immersed in the same bath. The bulb of the air thermometer was a long cylinder of glass, and its linear expansion was measured by direct observation.

The inference of the cubical expansion of one piece of glass from the linear expansion of another is a procedure which is scarcely

[1] *Mémoires de Lavoisier*, tom. i. p. 308.

allowable in very accurate scientific work, owing to the difference in the properties of different specimens of the same substance, arising from impurities and previous treatment. We have seen that all solids are more or less, and glass especially, subject to this malady. It is desirable, therefore, that some method should be devised for measuring the expansion of liquids, which does not involve the expansion of the enclosing envelope.

Such a method is afforded by the comparison of the densities of the liquid at different temperatures. Thus, if V_0 and ρ_0 denote the volume and density of a given mass of the liquid at 0°, and V and ρ the volume and density of the same mass at any other temperature θ, we have

$$V_0\rho_0 = V\rho.$$

But since

$$V = V_0(1+\alpha\theta),$$

it follows that

$$1+\alpha\theta = \frac{\rho_0}{\rho}.$$

Here, then, we have the means of determining the coefficient of absolute expansion of any liquid by simply comparing its densities at two different temperatures. There are two general methods of comparing the densities of liquids. The first depends on weighing equal volumes of the liquids, or on weighing a solid in the liquids and observing the loss of weight. In this method the expansion of the solid would again appear and complicate the operation.

The ratio of the densities of two liquids can, however, be determined directly by balancing a column of one against a column of the other in a U-tube; their densities are then in the inverse ratio of the heights of the corresponding columns above their common interface. This method may, therefore, be applied to compare the densities of two columns of the same liquid at different temperatures. It is founded on the principle stated by Boyle, that if the pressures of two columns of the same liquid at different temperatures are equal, their heights are inversely as their densities. By this means, then, the complications introduced by the expansion of the vessel in which it is necessary to enclose the liquid, are entirely got rid of.

102. Method of Equilibrating Columns—Experiments of Dulong and Petit.—The principle of the method of equilibrating columns, as adopted by Dulong and Petit,[1] in their experiments on the absolute expansion of mercury, is illustrated in Fig. 31. The mercury to be experimented on is contained in a two-arm tube, AA′ BB′, one arm of which, AA′, is kept in a chamber filled with broken ice, and the other,

[1] Dulong and Petit, *Ann. de Chimie et de Physique*, 2e tom. vii. p. 113, 1817.

BB′, is surrounded by a bath which can be heated to any temperature desired. The cross-tube, A′B′, is much smaller in bore than the upper arms, and is arranged so that its axis is accurately horizontal. This being secured, the heights of the surfaces at A and B above the axis of the cross-tube, when equilibrium is attained, will be inversely as the densities of the mercury in the corresponding arms. Hence, if AA′ be at 0°, and BB′ at $\theta°$ C., we have

$$1+\alpha\theta=\frac{\rho_0}{\rho}=\frac{h}{h_0},$$

where h is the height of the surface B above the axis of the horizontal

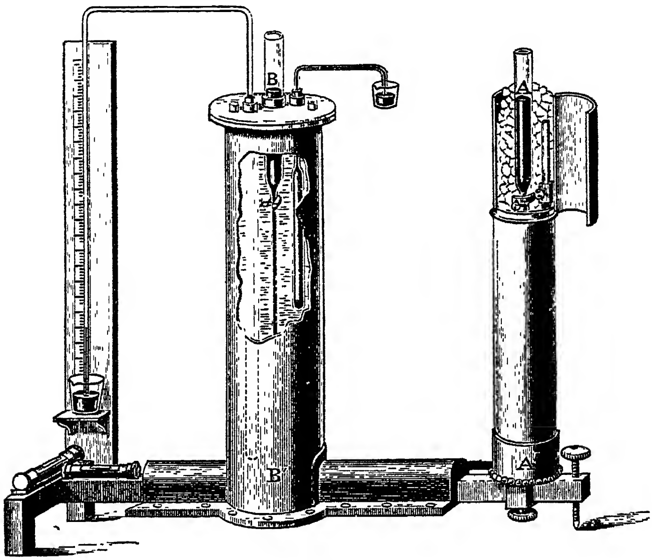


Fig. 31.

tube, and h_0 that of A above the same level. Hence the mean coefficient of absolute expansion of mercury between the temperatures 0° and $\theta°$ C. is given by the equation,

$$\alpha=\frac{h-h_0}{h_0\theta}.$$

The determination of α is thus reduced to the measurement of the heights h and h_0.

Strictly speaking, equilibrium is never secured in this experiment, for, on account of the difference of density, there will always be two feeble currents in the cross-tube—an upper current from the hot arm into the cold arm, and a lower current in the reverse direction. At

the level of the axis of the tube, equilibrium may, however, be regarded as existing, and it is for this reason that the heights h and h_0 are measured from the axis of this tube. In order to reduce this flow the bore of the horizontal tube is made narrow, but still wide enough to allow of equilibrium being freely established. The vertical branches, on the other hand, are about 2 cm. wide in their upper parts, so that no error may be caused in the difference of height $h - h_0$ by capillary depression. If these tubes were narrow, and yet of the same bore, such an error would be introduced into $h - h_0$ by the difference of temperature of the arms, for the capillary depression (or elevation) of a liquid in a tube depends on the temperature, being less at high than at low temperatures.

At the beginning of the experiment the arm AA′ was jacketed with ice, and the arm BB′ was encased in a copper cylinder containing oil, and heated by a furnace. Mercury was poured into the tubes till the free surface in the hot tube rose approximately into view above the bath chamber. When the temperature of the bath became stationary, a few drops of mercury at zero were added to the cold arm so as to bring the surface of the mercury in the warm arm into view over the top of the bath cylinder. A door in the ice jacket was then opened, and some of the ice removed, so that the surface of the mercury in the cold arm could be seen, and the heights h and h_0 determined. The temperature of the bath was registered by means of an air thermometer with a long cylindrical bulb, and also by a weight thermometer. The bulbs of these thermometers being long, they were supposed to indicate the mean temperature of the bath, and this was taken to be the average temperature of the mercury in the arm BB′.

The heights h and h_0 were determined by means of a specially constructed cathetometer, which read directly to $\frac{1}{20}$th mm., and by estimation to $\frac{1}{50}$th mm. The surface of the hot column was first observed, and then the surface of the cold column. This gave the difference of level $h - h_0$. The height h_0 was determined by measuring the distance between the surface of the mercury and a fixed reference mark near the top of the mercury column. This reference mark was carried by an iron rod which passed down through the ice jacket, and its distance from the axis of the cross-tube was determined accurately once for all.

At high temperatures the air and weight thermometers[1] gave

[1] In such an investigation as this it is of course illegitimate to employ a weight thermometer or any liquid-in-glass thermometer, unless it has been standardised by comparison with an air thermometer.

discordant results, so that the indications of the former were used exclusively by Dulong and Petit. The following table contains the results of their experiments. It gives the mean coefficient of expansion between 0° and 100°, 0° and 200°, 0° and 300°, on the air thermometer with the corresponding indications of the weight thermometer. Between 0° and 100° the coefficient is nearly constant, but it increases as the temperature becomes more elevated.

Air Thermometer.	Weight Thermometer	Mean Coefficient α.		
		max.	min.	mean.
0°	0°			
100°	100°	$\frac{1}{5547}$	$\frac{1}{5552}$	$\frac{1}{5550}$
200°	204°·61	$\frac{1}{5410}$	$\frac{1}{5431}$	$\frac{1}{5425}$
300°	314°·15	$\frac{1}{5289}$	$\frac{1}{5309}$	$\frac{1}{5300}$

In this form of the experiment it is not easy to secure that the mean temperature of the bath surrounding the thermometer bulb shall be the same as that surrounding the tube which contains the mercury, and from the method of heating the bath it is difficult to maintain its temperature stationary while the observations are being made, so that very great expedition is required in making the readings. Furthermore, it is essential that the air in the thermometer shall be perfectly dry, for if it contains any water vapour a considerable correction will become necessary at high temperatures. Finally, the value of the coefficient of dilatation of air (·00375), used by Dulong and Petit, was that deduced by Gay-Lussac, and was not sufficiently accurate.

For these reasons the determination of the coefficient of absolute expansion of mercury was undertaken by Regnault, on the same principle, but with improved apparatus, in which the errors of his predecessors were completely avoided. The close accordance of his results with those of Dulong and Petit shows, however, how excellently their experiments were conducted.

103. Regnault's Experiments.—In the form of apparatus employed by Dulong and Petit the chief source of uncertainty was the temperature of the bath, arising from the fact that being always filled to the top it could not be properly stirred to ensure uniformity of temperature throughout. A column of liquid heated from below may present great differences of temperature in different parts if not kept constantly stirred, and the difficulty is not entirely overcome by making the thermometer bulb the whole length of the bath, for even then

the temperature registered by the thermometer may not represent the mean temperature of the column of mercury situated in another part of the bath. Besides this source of error others occur in the direct observation of the summit of the warm column, which necessitates a little of the mercury being outside the bath, and it is also objectionable to have the surfaces of the two columns at different temperatures, as the surface tension will not be the same in both. The latter error is lessened, but not completely got rid of, by making the upper parts of the tubes wide. Besides this the columns were only about 50 or 60 cm. long, and the temperature of the column $h - h_0$ was not known with certainty.

For these reasons Regnault modified the apparatus in such a way that the bath could be constantly stirred, and its temperature kept uniform. Further, the surfaces of the mercurial columns which were

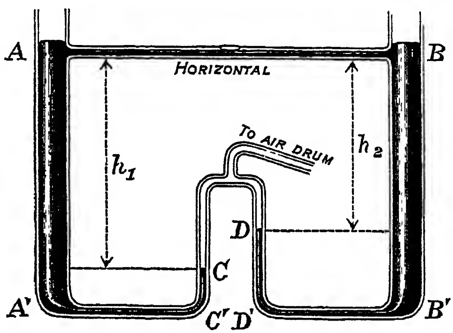


Fig. 32.

to be observed were enclosed in the same bath, and kept at a constant temperature.

The principle of the disposition of Regnault's apparatus is shown in Fig. 32. The vertical tubes AA′ and BB′ are made of iron, and are joined at their tops, A and B, by a horizontal cross-tube AB. The horizontal cross-tube joining the bottoms of AA′ and BB′ in the experiments of Dulong and Petit is here interrupted in its middle part at C′ and D′, where two vertical glass tubes, CC′ and DD′, are screwed in and connected with each other, and with a reservoir of air, which can be modified in pressure by means of an air-pump. In these glass-tubes the mercury stands at C and D, and at these surfaces the pressure is the same, viz. the pressure of the air in the reservoir. The long vertical tubes AA′ and BB′ are kept in baths at known temperatures, and the mercury in them is at a common level, viz. that of the horizontal communicating cross-tube AB. Hence if the temperatures be θ_1, and θ_2, while the

difference of level AC is h_1, and the height of B above D is h_2, we have

$$h_1(1+\alpha\theta_1)=h_2(1+\alpha\theta_2);$$

so that

$$\alpha=\frac{h_1-h_2}{h_2\theta_2-h_1\theta_1}.$$

The details of the apparatus are shown in Fig. 33.

The vertical tubes AA′ and BB′ were made of iron, and were

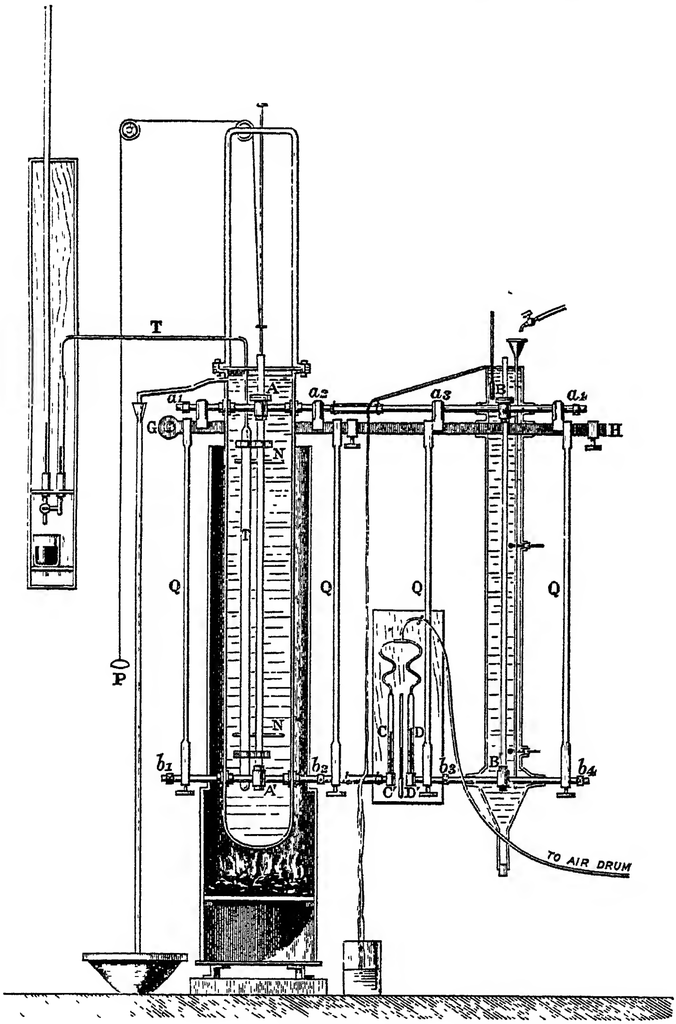


Fig. 33.

much longer than those used by Dulong and Petit, their length being

about 150 cm., and their diameter 1 cm. Their upper ends above the connecting cross-tube were open, so that the mercury could be introduced at will. One of them, BB′, was kept cold by a bath, through which a constant current of cold water circulated, and the horizontal arms were cooled both above and below by a stream of the same water. The other vertical tube AA′ was heated in a bath of oil, whose temperature was rendered uniform by means of agitators, NN worked by a cord P passing over a pulley.

The temperature was registered by means of an air thermometer, whose bulb extended throughout the whole length of the tube AA′. To support the apparatus and secure the horizontality of the cross-tube AB, Regnault attached it to a strong horizontal bar, GH, move-le round one extremity, G, and supported on two screws, one at its -lle and the other at its extremity, H. The cross-tube, AB, rested on it, and carried four brass rings, a_1, a_2, a_3, a_4, on which cross marks were traced to mark the axis of the tube, and these were arranged horizontally by observation of a cathetometer, and by adjustment of the controlling screws of the supporting bar, GH. From this bar ran also four metal rods, Q, Q, Q, Q, descending vertically, and supporting the lower parts of the apparatus, the points of attachment there being controlled by screws by which the lower cross-tubes could be made horizontal by means of marks, as in the case of the upper tube. In order to measure the heights h_1 and h_2 a small hole was drilled in the cross-tube, AB, and the pressure in the air reservoir was increased till the mercury rising in the tubes just began to overflow at this aperture.

As soon as this was secured the temperatures of the baths were noted as well as the heights of the mercury in the middle vertical tubes of glass, CC′ and DD′. Let H and H′ be the heights[1] in the long vertical tubes, and h and h' the heights in the short vertical tubes, and let θ be the temperature in AA′, and θ' the temperature in all the other tubes. Then we have the pressure of the air in the reservoir exceeding the pressure of the atmosphere by that due to AA′ minus that due to CC′, and this must be also equal to that due to BB′ minus that due to DD′; hence, denoting the coefficient of absolute expansion of mercury by m, we have—

$$\frac{H}{1+m\theta}-\frac{h}{1+m\theta'}=\frac{H'}{1+m\theta'}-\frac{h'}{1+m\theta'},$$

[1] H is the vertical height of the horizontal tube a_1, a_4 above b_1, b_2, and H′ the height of the same tube above b_3, b_4, while h and h' are the heights of surfaces at C and D above b_1, b_2, and b_3, b_4 respectively. If H = H′ for one temperature of the bath, then these heights will differ slightly for every other temperature, on account of the expansion of the tube AA′.

or

$$\frac{H}{1+m\theta}=\frac{H'+h-h'}{1+m\theta'}.$$

Hence

$$m=\frac{H'-H+h-h'}{\theta'H-\theta(H'+h-h')}.$$

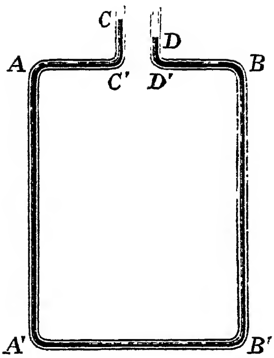


Fig. 34.

Second Form of the Apparatus.—M. Regnault also worked with another form of apparatus in which the lower cross-tube (Fig. 34) was uninterrupted, as in the apparatus of Dulong and Petit. The upper cross-tube was, however, interrupted by two vertical glass tubes CC′ and DD′, in which the mercury columns stood at levels C and D. The mercury columns are thus in direct equilibrium. The axis of the tubes AC′ and BD′ are horizontal, and at the same level, but the lower tube A′B′ is more or less inclined on account of the unequal dilatations of AA′ and BB′. On equating the pressures at the lowest part of the apparatus we have

$$\frac{H}{1+m\theta}+\frac{h}{1+m\theta'}+\frac{\epsilon}{1+m\theta'}=\frac{H'}{1+m\theta'}+\frac{h'}{1+m\theta'},$$

where ϵ is the small difference of level of the ends of A′B′. If the lower tube be horizontal $\epsilon=0$, and we have

$$\frac{H}{1+m\theta}=\frac{H'+h'-h}{1+m\theta'}.$$

Therefore

$$m=\frac{H'-H+h'-h}{\theta'H-\theta(H'+h'-h)}.$$

Regnault executed four series of experiments, which comprised in all about 130 observations, at temperatures varying between 25° C. and 350° C. The results of these experiments were then plotted graphically, and a curve traced which exhibited the relation between the temperature and the whole dilatation at any temperature. If m denotes the mean coefficient of expansion between 0° and θ, the whole dilatation per unit volume between these temperatures will be

$$\Delta_\theta=m\theta,$$

and if m be constant, the curve obtained by plotting the temperatures along the axis of x and the dilatation Δ along the axis of y will be a right line $y=mx$ inclined to the axis of x at an angle, whose tangent

is m. The curve obtained by Regnault was, however, not a right line, but was convex towards the axis of x, indicating that m increased with the temperature. Taking m to be of the form

$$m=a+b\theta,$$

the dilatation will be

$$\Delta_\theta=a\theta+b\theta^2,$$

and the curve will be parabolic.

Assuming the above formula to hold, the true coefficient of dilatation at any temperature will be

$$m_\theta=\frac{1}{V}\frac{dV}{d\theta},$$

where V is the bulk at θ° of the mass of unit volume at zero $= 1 + \Delta$ $= 1 + a\theta + b\theta^2$. Therefore

$$m_\theta=\frac{a+2b\theta}{1+a\theta+b\theta^2}.$$

The coefficient of expansion referred to the zero volume, or what we have termed the zero coefficient of expansion, is

$$m_0=\frac{1}{V_0}\frac{dV}{d\theta}=a+2b\theta.$$

The results of Regnault's experiments gave

$$a=0{\cdot}0001791,\ b=0{\cdot}000000025,$$

so that the mean coefficient of expansion of mercury was found to be

$$m=0{\cdot}0001791+0{\cdot}000000025\theta,$$

and the zero coefficient of expansion was found to be

$$m_0=0{\cdot}0001791+0{\cdot}00000005\theta.$$

Between 0° and 100° the coefficient m is sensibly constant, its value at 50° C. being $\frac{1}{5547}$. The corresponding value found by Dulong and Petit was $\frac{1}{5550}$.

104. Application of the Weight Thermometer.—Once the coefficient of absolute expansion of mercury is known, the weight thermometer may be applied with facility to the determination of the coefficients of absolute expansion of other liquids. For when the instrument is filled with mercury, a single observation gives us the apparent expansion of the mercury in the glass of the thermometer. Thus if w be the weight that flows over at θ and W_0 the weight that fills it at zero, we have

$$a=\frac{w}{\theta(W_0-w)},$$

consequently the coefficient of expansion of the glass g can be found from the equation

$$1+m=(1+a)(1+g),$$

where m is used to denote the coefficient of absolute expansion of mercury.

Liquids.

The coefficient g being known, the instrument can be filled with any other liquid, and its apparent coefficient a' determined in a similar manner. The real coefficient α of the liquid will then be found from the formula

$$1+\alpha=(1+a')(1+g).$$

Repeating the observations at various temperatures, the variation of α with temperature may be found, and the coefficients in the formula

$$\alpha=a+b\theta+c\theta^2$$

determined.

In a similar manner the weight thermometer may be employed to determine the cubical dilatation of solids. Thus, when the coefficient of absolute expansion of any liquid is known, a single observation gives the cubical dilatation of the material of which the bulb of the

Fig. 35.

Solids.

thermometer is constructed. It was in this manner that Dulong and Petit[1] first attempted to measure the coefficient of expansion of iron, knowing the absolute expansion of mercury, and using a weight thermometer with an iron bulb. They soon, however, abandoned this process for the more simple and general method of enclosing a bar of the solid under investigation inside the bulb of an ordinary weight thermometer made of glass, as shown in Fig. 35. In the case of solids which are not attacked by mercury no precautions are necessary, further than the attachment of bearings to the ends of the bar to keep it steady, and avoid fracture of the bulb. In the case of solids which are attacked by mercury, another liquid may be used, or their surfaces may be varnished or oxidised.

In all cases, it is necessary to know the weight W'_0 and the density ρ'_0 of the solid at zero. Its volume at zero is then W'_0/ρ'_0, and its volume at θ is

$$\frac{W'_0}{\rho'_0}(1+x\theta),$$

[1] Dulong and Petit, *Ann. de Chimie et de Physique*, 2e, tom. ii. p. 261, 1816.

where x is its coefficient of expansion. The remainder of the bulb and stem is filled with mercury. If W_0 and ρ_0 be the weight and density of this at zero, and if a quantity w flows over at θ, then the weight left in the bulb is $W_0 - w$, and its volume is

$$\frac{W_0 - w}{\rho_0}(1+m\theta).$$

Now the volume of the bulb at zero is

$$\frac{W_0}{\rho_0}+\frac{W'_0}{\rho'_0}.$$

Therefore its volume at θ is

$$\left(\frac{W_0}{\rho_0}+\frac{W'_0}{\rho'_0}\right)(1+g\theta).$$

Hence we have the equation

$$\left(\frac{W_0}{\rho_0}+\frac{W'_0}{\rho'_0}\right)(1+g\theta)=\frac{W'_0}{\rho'_0}(1+x\theta)+\frac{W_0-w}{\rho_0}(1+m\theta),$$

or finally

$$\left(\frac{W_0}{\rho_0}+\frac{W'_0}{\rho'_0}\right)g\theta=\frac{W'_0}{\rho'_0}x\theta+\frac{W_0}{\rho_0}m\theta-\frac{w}{\rho_0}(1+m\theta).$$

The quantities W_0/ρ_0, W'_0/ρ'_0, and w/ρ_0, are obviously the zero volume of the mercury contained in the instrument, the volume of the solid at zero, and the zero volume of the mercury which overflows.

Weight thermometer.

It is to be remarked that the sensibility of the weight thermometer diminishes with the density of the liquid employed, and also with its coefficient of expansion. For this reason the great density of mercury, and its tolerably large coefficient of expansion, recommend it especially for use in the weight thermometer. In addition, mercury does not evaporate sensibly, and in this respect possesses a great advantage over volatile liquids. When such liquids are employed, every precaution must be taken to prevent loss by evaporation. In such cases, however, it is better to dispense with the overflowing method, and adopt the following.

105. The Dilatometer—Application of the Ordinary Thermometer.—In the case of volatile liquids of small specific gravity, the accuracy obtained by reducing the observation to a weighing is more than counterbalanced in the weight thermometer by the errors introduced by evaporation. For this reason, the employment in these cases of an apparatus similar to the ordinary thermometer, as suggested by De Luc,[1] is preferable. The instrument (Fig. 36) is simply a large-bulbed thermometer, with an accurately-graduated stem, the volume of

[1] De Luc, *Recherches sur les Modifications de l'Atmosphère*, tom. ii. p. 124, etc.

the bulb and of each division of the stem being known. An experiment with mercury gives the coefficient of expansion of the instrument; and, when it contains any other liquid, two observations of the apparent volumes of the liquid at any two temperatures give the mean coefficient of apparent expansion between these temperatures.

Fig. 36.

This method is at once exceedingly simple and precise, and was employed by Kopp,[1] and also by M. Is. Pierre,[2] in their classical researches on the expansion of liquids.

106. Maximum Density of Water.—In the case of water a notable anomaly in the expansion is exhibited in the neighbourhood of 4° C. At, or very near, this point the liquid possesses a greater density than at any other temperature, and expands whether its temperature be raised or lowered. Thus water becomes specifically lighter in passing from 4° either up or down the scale, and the volume of any given mass is least at this temperature. The fact that ice forms on the top of water shows that water does not contract in volume continuously as the temperature falls to the freezing point. For if it contracted continuously to zero the liquid would be heaviest at this point, and freezing would begin at the bottom, and the ice would remain there unless solidification happened to be accompanied by increase of volume. This increase actually takes place in the case of water; but it has been proved that ice does not form first at the bottom of a pool, and afterwards float to the top.

Hope's experiment.

Hope's[3] well-known experiment places the whole process clearly in view. A tall glass beaker containing water is furnished with two thermometers, and an annular trough, as shown in Fig. 37. A freezing mixture of snow and salt is placed in the trough, and the water column is gradually cooled around its equatorial belt. While this cooling is in progress the indications of the thermometers are most interesting. Before the application of the freezing mixture the temperature registered by the upper thermometer slightly exceeds that of the lower, for the warmer and lighter portions of the water float to the top. The first effect of the freezing mixture is to reduce the lower thermometer to 4° C.

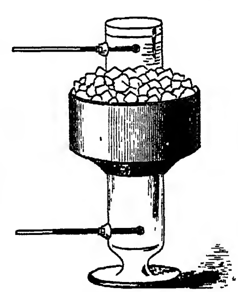


Fig. 37.

[1] Kopp, *Pogg. Ann.* Band lxxii., 1847.
[2] I. Pierre, *Ann. de Chimie et de Physique*, 3e, tom. xv., xix., xx., xxi., xxxi., xxxiii.
[3] Thos. Chas. Hope, *Ann. de Chimie*, 1re, tom. liii. p. 272, 1805.

without seriously affecting the upper. The lower thermometer now remains stationary, and the upper begins to fall rapidly till its temperature is reduced to zero, and ice begins to form on the top. The explanation is that water is heaviest at 4° C., and that it sinks as it cools, the layers which first reach 4° collecting at the bottom. After a certain stage certain layers become cooled below 4°, and the coldest parts rise through those which are less cold till ice forms on the top.

This property of water may also be well illustrated to a class by means of a float which rises to the surface in water near 4° C., and sinks when the temperature is a little above or below this point. The float may be constructed of a piece of glass tubing closed and so weighted that it will float in water at 4°, and sink in water at zero. A beaker of ice-cold water may be placed on the lecture table, with the float immersed, and lying at the bottom, the water not being dense enough to float it at zero. In the warm room, however, the temperature of the water begins to rise, the 4° layers sink to the bottom, and the float begins to creep towards the surface. Here it remains till the temperature passes 4°. The warmer layers now rise to the surface, and the float begins to sink gradually to the bottom.

It is on account of this property that a small pool of water on the surface of a glacier gradually eats its way into the ice, growing deeper and deeper with every return of the sun. Thus, if the whole mass of water in the pool is at zero, then, in the sunshine, the surface layer grows warm, and sinks to the bottom, where it melts another film of ice, and this process proceeds as long as the surface heat is supplied.

The anomalous expansion of water in the neighbourhood of 4° C. is a warning against the choice of any liquid as a standard thermometric substance. A thermometer filled with water would give the same indication, whether it grew warmer or colder from 4° C. In fact, the temperature at which the apparent volume of water in glass is least (or about what we call 5° C.) would be the lowest possible temperature attainable if water were the standard thermometric substance. Such an illustration shows us how utterly unintelligible and chaotic any system of thermometry founded on the expansion of a liquid might be.

107. Study of the Dilatation of Water.—The study of the dilatation of water has attracted much attention, not merely because of its anomalous behaviour at 4° C., but also because of the fact that water is the standard of density to which all other substances are referred. The unit of weight being defined as the weight of unit volume of water at some definite temperature and pressure, the variations of the density of water with temperature and pressure become a study of prime importance. It was in this connection that the first precise

experiments on the expansion of water were undertaken by Lefèvre-Gineau.[1] The method employed was by observing the loss of weight of a metallic cylinder when weighed in water at various temperatures. This method was also adopted by Hàlström who used a sphere of glass, and afterwards by Hagen and Matthiessen.

In the experiments of Hàlström,[2] the coefficient of linear expansion of a rod of glass was directly determined by the method of Ramsden, observations of the elongation being made at different temperatures between 0° and 30°. Any two of these observations are sufficient to determine the coefficients a and b in the formula

$$l=l_0(1+a\theta+b\theta^2),$$

and when these are known the volume V at any temperature $\theta°$ is given by the equation

$$V=V_0(1+a\theta+b\theta^2)^3.$$

For the glass rod Hàlström found the values

$$a=0\cdot000001960,\quad b=0\cdot000000105,$$

and he assumed that the same values would apply to the expansion of the glass sphere used in the weighing experiments.

This supposition is not strictly allowable, and the expansion of the glass sphere should be determined directly by means of the weight thermometer, or otherwise, as was done by Matthiessen.

When the glass sphere, suspended by a fine platinum wire from a pan of a balance, and counterpoised, is immersed in water, the weight required to be added to the pan to restore equilibrium is the weight of the volume V of water displaced by the sphere. Denoting this by W, we have W some function of the temperature depending both on the expansion of the glass and on that of the water. Thus we may write

$$W=W_0(1+\alpha\theta+\beta\theta^2+\gamma\theta^3+\ \ldots\ ).$$

By means of experiments at different temperatures Hàlström found

$$\alpha=+0\cdot000058815,\quad \beta=-0\cdot0000062168,\quad \gamma=+0\cdot00000001443.$$

Now the density ρ of water at any temperature θ is given by the formula

$$\rho=\frac{W}{V}=\frac{W_0}{V_0}\frac{1+\alpha\theta+\beta\theta^2+\gamma\theta^3}{(1+a\theta+b\theta^2)^3}=\rho_0(1+l\theta+m\theta^2+n\theta^3),$$

where the coefficients l, m, n are known in terms of α, β, γ, and a, b.

The density will be a maximum when

$$\frac{d\rho}{d\theta}=0,$$

[1] Lefèvre-Gineau, *Expériences faites pour déterminer la valeur du gramme.* See report in the *Journal de Physique de Delamétherie,* tom. xlix. p. 161.

[2] Hàlström, *Ann. de Chimie et de Phys.*, 2e, tom. xxviii. p. 56, 1825.

which gives the equation

$$3n\theta^2+2m\theta+l=0.$$

This equation gives two values of θ, one of which lies outside the limits of temperature, to which the above formulæ apply, and the other being equal to 4°·108 C. The coefficients l, m, and n were

$$l=0\cdot000052939,\quad m=-0\cdot0000065322,\quad n=0\cdot00000001445.$$

The following table gives the volume at various temperatures up to 30° of a mass possessing unit volume at zero, according to Hälström :—

Temperature.	Volume.	Temperature.	Volume.
0°	1·0000000	8°	0·9999872
1°	0·9999536	9°	1·0000421
2°	0·9999202	15°	1·0006273
3°	0·9998996	20°	1·0014406
4°	0·9998818	25°	1·0025398
4°·1	0·99989177	30°	1·003916
5°	0·9998968	...	...

According to this table the maximum density would appear to be somewhat above 4° C.; but as the variation is small in the neighbourhood of a maximum it is difficult to fix the temperature of maximum density with absolute precision.

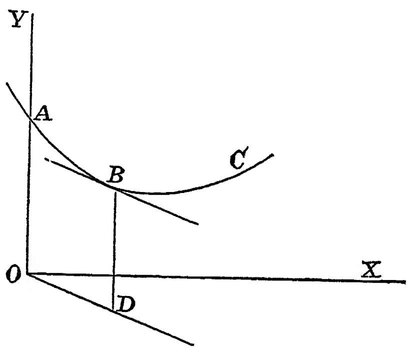


Fig. 38.—Despretz's first method.

Most of the other experimenters in this subject have proceeded by the dilatometer or ordinary thermometer method (Art. 105). By this method Despretz[1] plotted a curve, the ordinates of which represented the apparent volume in glass, and the corresponding abscissæ the temperature. This curve is approximately parabolic, as shown in Fig. 38, the vertex of the parabola corresponding to the temperature of about 5° C. This then is the temperature of least apparent volume. The real volume of the water at any temperature may be found by adding to the corresponding ordinate of this curve the dilatation of the glass. For this purpose it is only necessary to construct a curve below OX representing the dilatation of the glass. If the glass be supposed to expand uniformly through the range of temperature employed, this curve will be a right line OD, such that,

[1] Despretz, *Ann. de Chimie et de Physique*, 2e, tom. lxx. p. 5; tom. lxxiii. p. 296, 1840.

if v be the volume at θ°, and v_0 the volume at 0°, the dilatation of the glass will be $v - v_0 = v_0 g\theta$, and therefore[1] the tangent of the angle DOX will be $v_0 g$, where g is the mean coefficient of expansion of the glass, and is determined by a previous experiment by the method already indicated in Art. 104. The vertical ordinate intercepted between the curve ABC and the line OD will therefore represent the real volume of the water at the corresponding temperature. Hence, to obtain the temperature of least volume it is only necessary to find

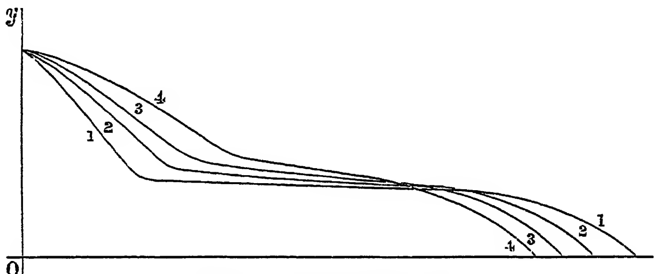


Fig. 39.—Despretz's second method.

the least ordinate between ABC and OD. This is done by drawing a line parallel to OD so as to touch the curve ABC, and the corresponding ordinate BD cuts the axis OX at a point which corresponds to the temperature of maximum density.

In these experiments when the water was pure and free from air, it did not solidify at zero; but remained liquid to $-20°$ C. The curve ABC could accordingly be continued far below zero, and it showed that at these low temperatures the water continued to increase in volume up to the point of solidification. The sudden change of volume of water in solidifying at zero is thus merely a leap replacing the gradual change which is here shown to occur.

A form of experiment very similar to Hope's was also conducted by Despretz. A beaker of water furnished with four thermometers, as in Hope's experiment, was allowed to cool in a cold atmosphere, and the indications of the thermometers were carefully noted. A curve was constructed for each thermometer (Fig. 39), showing its variations of temperature, the time being measured along the axis of x and the corresponding temperatures parallel to the axis of y. The lowest thermometer (1) fell most rapidly in temperature at first, and the highest (4) most slowly. The lowest then remained stationary at 4°, while the others gradually fell, the highest falling most rapidly till its temperature became zero. The curve appertaining to the lowest thermometer was thus at first below the others, and was cut by

[1] v_0 is the apparent volume of the water.

them at 4°, and this thermometer was the last to attain to zero. The mean result obtained by Despretz by the first method was 4°·007, and by the second 3°·997. Numbers agreeing very closely with these were obtained by other experimenters. Thus Hälstrom found 4°·108, H. Kopp 4°·08, and Is. Pierre 3°·92. From these numbers we may conclude that 4° C. represents very approximately the temperature of the maximum density of water. A general table of the results of various observers will be found in Rosetti's[1] memoirs on the dilatation of distilled water. The following table contains Rosetti's results from − 10° to + 100° C., the volume being taken equal to unity at the freezing point :—

$\theta°$.	V.	$\theta°$.	V.	$\theta°$.	V.	$\theta°$.	V.
− 10	1·001729	18	1·001219	46	1·01001	74	1·02490
− 9	1449	19	1431	47	1044	75	2553
− 8	1191	20	1615	48	1088	76	2617
− 7	0963	21	1828	49	1134	77	2681
− 6	756	22	2049	50	1181	78	2745
− 5	573	23	2276	51	1229	79	2809
− 4	416	24	2511	52	1278	80	2874
− 3	218	25	2759	53	1327	81	2939
− 2	168	26	3014	54	1376	82	3005
− 1	74	27	3278	55	1425	83	3072
0	1·000000	28	3553	56	1474	84	3139
1	0 999943	29	3835	57	1524	85	3207
2	920	30	4123	58	1574	86	3276
3	880	31	1·00442	59	1625	87	3345
4	871	32	473	60	1677	88	3414
5	881	33	505	61	1731	89	3484
6	901	34	538	62	1785	90	3554
7	938	35	572	63	1839	91	3625
8	985	36	608	64	1895	92	3697
9	1·000047	37	645	65	1951	93	3770
10	124	38	682	66	2008	94	3844
11	216	39	719	67	2065	95	3918
12	322	40	757	68	2124	96	3993
13	441	41	796	69	2183	97	4069
14	572	42	836	70	2243	98	4145
15	712	43	876	71	2303	99	4222
16	870	44	917	72	2365	100	4300
17	1031	45	958	73	2427	..	...

The foregoing results apply to the case of water under the pressure of one atmosphere. When the pressure is increased the temperature of maximum density recedes towards zero, and in a recent series of experiments, M. Amagat[2] finds the mean rate of retrogression to be about 0°·025 C. per atmosphere increase of pressure. Thus under the

[1] Rosetti, *Ann. de Chim. et de Phys.*, 4e, tom. x. p. 461 ; tom. xvii. p. 370, 1867-69.

[2] Amagat, *Comptes Rendus*, 1st May 1893, tom. cxvi. p. 946. The diagrams illustrating the results of these experiments are exceedingly interesting.

pressures 41·6, 93·3, 144·8 atmos. the temperatures of greatest density were found to be 3°·3, 2°·0, and 0°·6 respectively.

108. Empirical Formulæ.—Various empirical formulæ have been proposed to represent the expansion of liquids. In the case of water, Kopp used the formula

$$V = 1 - a\theta + b\theta^2 - c\theta^3$$

for the volume at any temperature θ of a mass occupying unit volume at zero.

Matthiessen, taking the volume to be unity at 4° C., adopted the formula between + 4° and 32°

$$V = 1 - a(\theta - 4) + b(\theta - 4)^2 - c(\theta - 4)^3,$$

where

$$a = 0{\cdot}00000253, \quad b = 0\ 000008389, \quad c = 0{\cdot}00000007173,$$

and for temperatures between 32 and 100, the formula

$$V = 0{\cdot}999695\theta + 0{\cdot}0000054724\theta^2 - 0{\cdot}000000011126\theta^3.$$

M. Rosetti in turn adopted a formula of the more general form

$$V = 1 + a(\theta - 4)^\alpha + b(\theta - 4)^\beta + c(\theta - 4)^\gamma.$$

Such formulæ, however, can scarcely be regarded as having any theoretic importance. They merely represent more or less approximately the general results of experiments from which their constants have been determined, and their value depends upon how closely they represent the whole series of experiments.

Recently D. Mendeléeff[1] has proposed a formula for the density of water between − 10° and + 200° C. of the form

$$\rho = 1 - \frac{(\theta - 4)^2}{(A + \theta)(B - \theta)C},$$

the density at 4° being unity. A general formula, supposed to apply to all liquids, had been previously given by the same physicist[2] giving the density at any temperature θ in the form

$$\rho = \rho_0(1 - k\theta).$$

Such a formula, of course, cannot embrace such cases as the anomalous expansion of water at 4°, for unless k be supposed also a function of the temperature, the density will continually decrease as the temperature rises. General doubt has been thrown on even the limited application of this formula by various authors, especially by Avenarius and Grimaldi.[3] The latter found that the formula

$$v = a + b \log(\theta_c - \theta)$$

[1] D. Mendeléeff, *Phil. Mag.*, January 1892, p. 29.

[2] *Russian Physico-Chem. Soc. Journal*, 1884.

[3] S. P. Grimaldi, *Journal de Physique*, tom. v. p. 29, 1886.

proposed by Avenarius represented the results of his experiments very approximately. In this formula θ_c represents the critical temperature of the liquid (see Art. 209).

Other general formulæ[1] connecting pressure, volume, and temperature, especially those of Clausius and Van der Waals, will be considered later on (Chapter V. section vii.).

109. Maximum Density of Saline Solutions.—It was established by Despretz[2] that other liquids, especially saline solutions, exhibit temperatures of maximum density under a given pressure. The solutions were observed in the dilatometer, and in this they could be reduced in the liquid state to temperatures considerably below their normal freezing points, and their variations of volume could be noted as in the case of water. The effect of salts dissolved in water is to notably lower the temperature of maximum density, as well as the normal freezing point. The following table, taken from Rosetti's memoir,[3] fully exhibits this point in the case of ordinary salt:—

SOLUTIONS OF COMMON SALT (NaCl.)

Weight °/. of Salt w.	Max Density Temperature θm	Normal Freezing Point θo.	Lowering of θm $=\Delta\theta m$.	$\frac{\Delta\theta m}{w}$.	$\frac{\theta o}{w}$.
0	+ 4°	0°	0	...	...
0·5	+ 3	−0·32	− 1·00	−2·00	−0·64
·1	+ 1·77	−0·65	− 2·23	−2·23	−0·65
·2	− 0·58	−1·72	− 4·58	−2·29	−0·63
·3	− 3·24	−1·90	− 7·24	−2·41	−0·63
·4	− 5·63	−2·60	− 9·63	−2·41	−0·65
·6	−11·07	−3·91	−15·07	−2·51	−0·65
·7	−13·69	−4·60	−17·69	−2·53	−0 65
·8	−16·62	−5·12	−20·62	−2·58	−0·64
A specimen of sea-water	− 3·21	−1·90	...	...	...

The last two columns show that the lowering of the normal freezing

[1] M. P. de Heen (*Journal de Phys.* tom. iii. p. 549, 1884), assuming that the molecules of a liquid attract according to the inverse seventh power of the distance, deduces the formula $v=(1-1\cdot333a\theta)-\frac{1}{1\cdot333}$, where a is the coefficient of expansion at zero.

Rankine proposed the formula

$$\log v=-\mathrm{A}+\mathrm{B}\Theta+\frac{\mathrm{C}}{\Theta},$$

where v is the volume, and Θ the absolute temperature (*Edin. New Phil. Journal*, October 1849; *Scientific Papers*, p. 13).

[2] Despretz, *Ann. de Chimie et de Phys.*, 2e, tom. lxx. p. 49, 1839.

[3] Rosetti, *Ann. de Chimie et de Phys.*, 4e, tom. xvii. p. 382, 1869.

point, as well as that of the temperature of maximum density, is within the range of these experiments approximately proportional to the quantity of salt dissolved.

110. Dilatation of Liquids at Temperatures above the Normal Boiling Point.—The normal boiling point of a liquid is the temperature at which it boils under the pressure of one standard atmosphere. Under this pressure the substance remains in the liquid state, only up to the boiling point, and is then vaporised with a sudden and large change of volume. By increasing the pressure, however, ebullition may be prevented indefinitely, and the substance may be maintained in the liquid state up to a certain temperature (called the critical temperature), at which it *appears* to be completely and suddenly vaporised.[1]

For the present it is sufficient to know that a liquid may be maintained at temperatures far above its normal boiling point, and that consequently its expansion may be investigated at high temperatures. In general, the coefficient of expansion of a liquid increases with the temperature, and at temperatures which are high for a liquid—that is, temperatures near the critical temperature of that liquid—the coefficient of expansion may equal or exceed that of the permanent gases. Thus Thilorier[2] found that liquid carbonic acid expanded between zero and 30° by half its volume at zero, which shows an expansion four times greater than that of air, and Drion[3] obtained similar results for ether, sulphurous acid, and nitrous acid, as shown in the following table :—

COEFFICIENTS OF EXPANSION

Temperature.	Ether.	Sulphurous Acid.	Nitrous Acid.
0°	0·001482	0·001734	0·001445
10	0·001568	0·001878	0·001514
30	0·001811	0·002192	0·001706
50	0·002065	0·002535	0·002021
70	0·002390	0·003176	0·002478
90	0·002910	0·004147	0·003081
110	0·003690	0·005919	...
130	0·005031	0·009571	...

Thus at about 110° ether has a coefficient of expansion equal to that

[1] This transformation is considered in Chapter V. Section vi.

[2] Thilorier, *Ann. de Chimie et de Phys.*, 2e, tom. lx. p. 427, 1835.

[3] Drion, *Ann. de Chimie et de Phys.*, 3e, tom. lvi. p. 5, 1859.

of air (0·003665), and sulphurous and nitrous acids attain the same value about 80° and 105° respectively.

A series of experiments was executed by Hirn[1] on the same subject, with a modified form of the weight thermometer, consisting of a huge bulb containing the liquid, and a long stem containing mercury which overflowed at a point 11·25 m. above the bulb, so that the liquid expanded under a constant pressure of nearly 15 atmospheres.

He expressed the dilatation Δ by means of formulæ of the type

$$\Delta = a\theta + b\theta^2 + c\theta^3 + d\theta^4,$$

and found that the coefficient of expansion of water at 180° C. was about half that of air, while that of alcohol at 160° was 0·017843, or about five times greater than that of air. Thus in the case of water, the volume being taken equal to unity at zero, the volume at any temperature θ between 100° and 200° C. was given by the formula

$$v = 1 + 0{\cdot}00010867875\theta + 0{\cdot}0000030073653\theta^2$$
$$+ 0{\cdot}0000000028730422\theta^3 - 0{\cdot}0000000000066457031\theta^4,$$

with similar formula for alcohol, ether, and other substances.

More recently M. S. P. Grimaldi[2] has executed a series of experiments on the dilatation of ethyl oxide under pressures varying from 1 to 25 metres of mercury, and at temperatures between 0° and 105° C., the pressure being produced by the electrolysis of acidulated water. From the dilatations the compressibility was deduced, and was found to be independent of the pressure in accordance with the observations of Jamin, Amaury, Deschamp, and Cailletet, but contrary to the experiments of Colladon and Sturm, as well as those of M. Amagat. From the experiments of Grassi it would, however, appear that the compressibility of water increases as the temperature falls, so that the temperature of maximum density is lowered by increase of pressure, the lowering being about 1° C. for a pressure of about 50 atmospheres (see further, Art. 107).

[1] Hirn, *Ann. de Chimie et de Phys.*, 4e, tom. x. p. 32, 1867.

[2] Grimaldi, *Journal de Physique*, tom. v. p. 29, 1886.

SECTION III

DILATATION OF GASES

111. Dilatation of the Thermometric Substance.—Having agreed to measure equal increments of temperature by equal absolute increments of volume of some chosen substance under constant pressure, we have already seen that for this substance the equation

$$V = V_0(1 + \alpha\theta)$$

always holds true, where α is a constant, namely, the coefficient of expansion of the substance at the chosen zero of temperature, or the mean coefficient of expansion between zero and θ. In order to determine α for the thermometric substance it is necessary to observe the volume V_0 at zero and the absolute increase of volume $V - V_0$ corresponding to any temperature θ, or if the volume v of a degree measure be known we have simply $\alpha = v/V_0$. The practical determination of α consequently requires an accurate knowledge of the expansion of the envelope, and this may be found by the methods already described.

These remarks apply to the thermometric substance whatever it may be. For this substance the relation between any two temperatures and the corresponding volumes will always be, under the given conditions of pressure,

$$\theta - \theta' = A(v - v'),$$

which merely expresses that the change of temperature is proportional to the change of volume. The factor A is a constant under given conditions of pressure, and is therefore a function of the pressure only, which can be determined when the laws of compressibility of the substance are known. If the thermometric substance happened to be a liquid at all temperatures obtainable, and if it reached a least volume v_0 at some temperature (like water at 4°), then this would correspond to the lowest temperature which it would be possible to register with this substance. Taking this as our zero, the temperature measured

from this zero might be called the absolute temperature for this substance, and we would have

$$\Theta = A(v - v_0).$$

For many reasons, already mentioned, it has been decided to take some permanent gas as the standard thermometric substance. The ideal limit to which such a substance approximates is exact obedience to Boyle's law. If this law is obeyed, it follows that the product of the pressure and volume is proportional to the temperature measured from the absolute zero of an ideal thermometer filled with a substance, always obeying Boyle's law, so that the volume v_0 is zero, and the constant A is proportional to the pressure. Hence for all such substances when temperature is measured in this manner, we have the equation

$$pv = R\Theta.$$

If $\theta°$ be the corresponding temperature on the centigrade scale, and Θ_0 the absolute temperature corresponding to the melting point of ice, then

$$\Theta = \Theta_0 + \theta.$$

Let us now seek the mean coefficient of expansion of such a substance. In working with solids and liquids it was not necessary to consider small variations of pressure. A small change of pressure does not sensibly affect the volume of a solid or liquid. In the case of gases, however, variations of pressure notably affect the volume, and in all practical investigations such changes must be determined and allowed for.

In the first place, let us suppose that the pressure is maintained constant, and that the temperature and volume vary. At any temperature $\theta°$ C. we have the equation

$$pv = R\Theta,$$

and at 0° C. we have

$$pv_0 = R\Theta_0,$$

consequently

$$\frac{v - v_0}{v_0} = \frac{\Theta - \Theta_0}{\Theta_0} = \frac{\theta}{\Theta_0},$$

and therefore

$$\alpha = \frac{v - v_0}{v_0 \theta} = \frac{1}{\Theta_0},$$

Hence the relation between the absolute temperature Θ and the centigrade temperature θ is

$$\Theta = \Theta_0 + \theta = \frac{1}{\alpha} + \theta.$$

It thus appears that the mean coefficient of expansion between 0° and $\theta°$ C. of any thermometric substance obeying Boyle's law is the

reciprocal of the absolute temperature of the freezing point. This coefficient is independent of R, that is, of the other properties of the substance, and it therefore follows that if all the gases obey Boyle's law, and if they all give the same absolute zero when used as a thermometric substance, they will all possess the same coefficient of expansion, and *vice versâ*. The whole question about gases, then, reduces to the examination of how closely they obey Boyle's law. This point will be considered in Art. 218. At present we shall consider the methods by which the mean coefficient a has been obtained in the case of ordinary gases. There are in general two methods of attack. Either by keeping the pressure constant and observing the change of volume between 0° and 100° C. (or any other temperature θ° C.), or by keeping the volume constant and noting the corresponding change of pressure. The former gives the mean coefficient of increase of volume, or the dilatation in the proper sense of the term, while the latter gives the coefficient of increase of pressure. If Boyle's law is obeyed these two coefficients are equal, for the former is

$$\frac{v-v_0}{\theta v_0}=\frac{1}{\Theta_0},$$

and the volume being constant the latter is

$$\frac{p-p_0}{\theta p_0}=\frac{1}{\Theta_0}.$$

In general, when the pressure is kept constant, we have

$$\frac{1}{v}\frac{dv}{d\theta}=\frac{1}{\Theta},\quad \frac{1}{v_0}\frac{dv}{d\theta}=\frac{1}{\Theta_0}.$$

Similarly when the volume is kept constant,

$$\frac{1}{p}\frac{dp}{d\theta}=\frac{1}{\Theta},\quad \frac{1}{p_0}\frac{dp}{d\theta}=\frac{1}{\Theta_0}.$$

The extent to which the coefficient of increase of pressure is found by experiment to agree with the coefficient of increase of volume will consequently furnish a test as to how nearly the gas under examination obeys Boyle's law.

112. Dilatation under Constant Pressure.—The coefficient of expansion of the thermometric substance must be determined by directly observing its volume under constant pressure at two fixed temperatures, unless some law connecting the pressure and volume at constant temperatures has been previously established. If such a law be known other methods in which the pressure is variable and volume constant, or in which both pressure and volume vary, may be devised. If

Boyle's law had not been known all experiments on the expansion of gases would have been made by observing the volume under constant pressure. As a matter of fact, this method was adopted in the earlier investigations, but it was ultimately superseded by other methods depending on the application of Boyle's law. The practical difficulties attending the observation of the volume under constant pressure, and the errors attending the experiment, are much greater than those attending the observation of the pressure under constant volume. Nevertheless, it is of prime importance that the coefficient of expansion under constant pressure should be measured by direct experiment, and the comparison of this coefficient with that obtained by any other method founded on some previously-determined pressure-volume-rela-

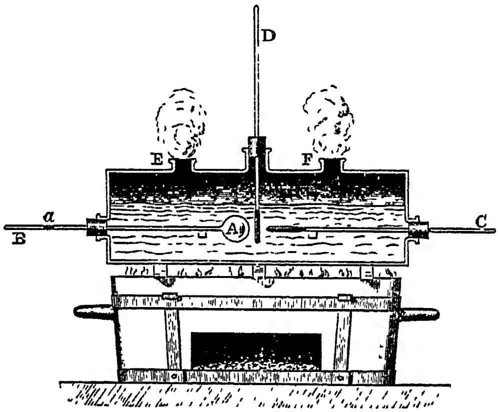


Fig. 40.—Gay-Lussac's Apparatus.

tion at constant temperature, will furnish a test of the truth and range of applicability of this relation.

The early experimenters on this subject were not aware of the great importance of procuring the air, or other gas, quite pure and perfectly free from aqueous vapour. Gay-Lussac[1] seems to have been the first to pay some attention to this important point. The apparatus (Fig. 40) employed by this philosopher was simply a glass bulb, A, furnished with a straight stem, AB, which was carefully calibrated. The air which filled the bulb was freed from moisture by being passed through desiccating tubes before entering the bulb. The bulb was first filled with mercury and then turned upside down, so that the mercury escaped and air entered through the drying tubes to take its place. A short index *a* of mercury was left in the stem to mark the volume of the air enclosed. The stem was maintained horizontal, so

[1] Gay-Lussac, *Ann. de Chimie et de Physique*, 1re, tom. xliii. p. 137, An Xe.

that the pressure of the enclosed air was that of the atmosphere. By reading the barometer it can be ascertained if this remains constant during the experiment; if not, corresponding corrections must be applied for the variation of volume arising from change of pressure. The bulb and part of the stem were immersed in melting ice and afterwards in boiling water, the temperature of which was noted by mercury thermometers. The volume was noted in both cases, and the mean coefficient of expansion deduced was 0·00375. Correction, of course, must be made in such an experiment for the expansion of the glass. The volume of the bulb and of each division of the stem at some definite temperature is ascertained by weighing the quantity of mercury it contains at this temperature, and from the known expansion of the glass the volume at any other temperature can be calculated.

Gay-Lussac.

The same value for this coefficient was independently arrived at by Dalton,[1] and afterwards these experiments were repeated and confirmed by Dulong and Petit,[2] and consequently this value of the coefficient was universally accepted as correct until Rudberg, a Swedish physicist, published a memoir giving the lower value 0·003646. Rudberg here pointed out the great importance of thoroughly desiccating not only the air admitted to the bulb, but also the bulb itself. For this purpose the bulb was repeatedly filled with dry air and exhausted, while at the same time it was highly heated so as to expel all moisture from its walls. The experiments of Rudberg were, however, conducted at constant volume, so that Magnus[3] undertook the re-determination of the coefficient of expansion under constant pressure by the method of Gay-Lussac. The mean of thirty-two experiments gave a value differing little from that of Gay-Lussac, the extreme values being 0·0038769 and 0·00355. The great divergence exhibited here led Magnus to

Rudberg.

Magnus.

[1] Dalton found that 1000 measures of air at 55° F. became 1325 at 212° F. (*Memoirs of the Manchester Phil. Soc.*, vol. v. pt. iii. p. 599), and in his *Chemical Philosophy* he states that 1000 measures at 33° F. become 1376 at 212°, according to his own and Gay-Lussac's experiments. Regnault appears to have mistaken Dalton's meaning and fancied that an error had crept in here, for he says (*Mémoires de l'Académie*): "Rudberg termine son Second Mémoire par une remarque importante, qui avait été déjà faite en 1813 par Gilbert (*Annales de Gilbert*, tom. xiv. p. 267), mais qui depuis était tombée tout à fait dans l'oubli; savoir, que les expériences de MM. Dalton et Gay-Lussac, que l'on avait regardées comme ayant donné des résultats presque identiques, différent, au contraire, beaucoup."

This statement arose from the supposition that Dalton took the initial volume to be 1000 at 32° F. instead of 55° F. He, however, expressly states that when the volume was 1000 at 55° F. it was 1325 at 212°, and he mentions in addition that he had not the means of obtaining the volume at 32° F. The coefficient is thus 0·00373, which is sensibly the same as the mean of Gay-Lussac's experiments.

[2] Dulong and Petit, *Ann. de Chimie et de Physique*, 2e, tom. ii. p. 240, 1816.

[3] Magnus, *Pogg. Ann.* vol. lv., 1842; *Ann. de Chim. et de Phys.*, 3e, tom. vi. p. 330.

abandon the method of Gay-Lussac altogether. This method suffers from defects which render the results obtained by it open to doubt, even though the air enclosed by Gay-Lussac had been perfectly dry. These defects lie in the method of measuring the volume of the air by means of a moving index of mercury. In the first place, it may be objected that the index does not properly close the tube so as to prevent all communication between the air inside and outside.[1] Magnus, in fact, found that when the apparatus was brought to zero the air enclosed scarcely ever exhibited the same volume. Besides this a mercury index always sticks somewhat to the walls of the tube, so that the pressure inside and outside may differ somewhat without moving the index. The errors arising from these sources are consequently sufficient to condemn the method.

113. Regnault's Experiments.—After executing several series of experiments by other methods depending on the application of Boyle's law to gases, Regnault next attacked the problem of directly determining the expansion under constant pressure. For this purpose he employed the apparatus shown in Fig. 18, which may be termed a constant pressure air thermometer. The bulb was well dried and filled with dry air at the pressure of the atmosphere, the mercury being adjusted so as to stand at a fixed mark a on the arm FG, and at the same level on the other arm, IJ, of the manometer. The tube *op* (Fig. 17) was then sealed up while the bulb was surrounded with melting ice. The bulb at this stage contained air at zero, and the pressure H of the atmosphere, which was determined by reading the barometer at the time of sealing the tube *op*. The ice was then removed, and the bulb was placed in a steam bath, the mercury being allowed to escape from the manometer till equality of level, or a small difference of level h', which was measured by means of a cathetometer, was secured.

[1] Regnault (*Ann. de Chim. et de Phys.*, 3e, tom. iv. p. 43, 1842) also made some experiments on the expansion of air by the method of Gay-Lussac, and obtained the numbers

0·003641, 0·003626, 0·003635, 0·003647, 0·003552.

All these numbers are less than those obtained by other methods, and this Regnault considers remarkable. This might arise from the imperfect closing of the stem by the mercury index. Thus if the index does not slide air-tight in the stem, then when the gas is expanding the internal pressure is greater than the external, and some air will escape from the bulb, and the final volume will appear too small. So again when the air is contracting the external pressure exceeds the internal, and air enters the bulb. In the first process warm air escapes, and in the second cold denser air enters, so that when the apparatus again returns to zero the volume of the air enclosed would be greater than before. In an experiment the index at zero stood at the division 152·7, and at 100 the reading was 534·5, and after returning to zero the reading was 154·5, the barometer not having sensibly changed.

During this process the air expanded and occupied part of the graduated arm FG. Let V_0 be the volume of the bulb at zero, v_1 the volume of the stem up to the fixed mark a, and v_2 the volume of the graduated tube from a to the surface of the mercury. Then if the whole mass of gas were at the same temperature its volume at zero would be $V_0 + v_1$ and its volume at θ would be $(V_0 + v_1 + v_2)(1 + g\theta)$, and if the pressure were exactly the same in the second case as in the first the coefficient of expansion would be given at once by the equation

$$(V_0 + v_1)(1 + \alpha\theta) = (V_0 + v_1 + v_2)(1 + g\theta),$$

the temperature θ being approximately 100° C., the difference arising on account of the atmospheric pressure being not necessarily exactly 760 mm.

In the experiment, however, the gas occupying the stem and tube was not at the same temperature as that in the bulb, and the final pressure was not exactly the same as the initial. If the volume v_1 is at the temperature θ_1, and v_2 at θ_2, while the bulb is at θ and the initial and final pressures are $H + h$ and $H' + h'$, then the full equation for α will be

$$\left[\frac{V_0(1+g\theta)}{1+\alpha\theta} + \frac{v_1(1+g\theta_1)}{1+\alpha\theta_1} + \frac{v_2(1+g\theta_2)}{1+\alpha\theta_2}\right](H'+h') = \left[V_0 + \frac{v_1(1+g\theta_1)}{1+\alpha\theta_1}\right](H+h).$$

This equation follows from the application of the equation $\Sigma pv/(1 + \alpha\theta) =$ constant (Ex. 4, p. 141) for the whole mass of gas. From this we have Regnault's formula [1]

$$1+\alpha\theta = \frac{(H'+h')(1+g\theta)}{H+h+\frac{v}{V_0}\frac{H+h}{1+\alpha\theta_1} - \frac{v}{V_0}\frac{H'+h'}{1+\alpha\theta_1} - \frac{v'}{V_0}\frac{H'+h'}{1+\alpha\theta_2}},$$

where v is written for $v_1\ (1 + g\theta_1)$ and v' replaces the corresponding terms in θ_2 and v_2. The terms in the denomimator which embrace v and v' also include α, the quantity sought, but on account of the

[1] In this equation θ_1 and θ_2 are practically constant, while θ and v_2 vary. Hence differentiating with respect to θ we have

$$\frac{V_0 g}{1+\alpha\theta} - \frac{V_0\alpha(1+g\theta)}{(1+\alpha\theta)^2} + \left(\frac{1+g\theta_2}{1+\alpha\theta_2}\right)\frac{dv_2}{d\theta} = 0.$$

Hence

$$\frac{dv_2}{d\theta} = \frac{(1+\alpha\theta_2)(\alpha-g)V_0}{(1+g\theta_2)\ (1+\alpha\theta)^2}, \text{ which varies as } \frac{1}{\Theta^2}.$$

That is, the increase dv_2 of volume corresponding to a definite rise of temperature $d\theta$ varies inversely as the square of the absolute temperature. Hence the sensibility of the instrument decreases as the temperature rises, and this circumstance led Regnault to reject the constant pressure air thermometer. In the case of the constant volume thermometer, on the other hand, the sensibility is as good at high temperatures as at low

small values of v and v' compared with V_0, an approximate value of a may be used in these terms, and the resulting value of a deduced from the equation. In this experiment the accurate determination of the volumes V_0, v_1, and v_2 is of prime importance, as well as certain knowledge of the temperature θ_2 of the bath enclosing the manometer. The volumes are determined by weighing the mercury which fills the corresponding spaces at some definite temperature, and the temperature of the bath is kept uniform by constant agitation. Another point of importance is the thorough desiccation of the manometer tube FG as well as the bulb.

The value of a obtained in this manner slightly exceeds that obtained by the other methods, but the excess is not so notable as to lead to the conclusion that within the limits of the experiments Boyle's law is sensibly deviated from. The first series of experiments gave the same coefficient for air and hydrogen, but in the later experiments the coefficient for hydrogen was somewhat less than that of air. A similar result was obtained by Magnus.[1] The difference, however, was within the limits of experimental error, and consequently nothing definite could be inferred from it (cf. Art. 219).

By varying the initial pressure the expansion under different pressures may be examined in the same way. The results obtained by Regnault were as follows:—

EXPERIMENTS UNDER ATMOSPHERIC PRESSURE

Air	0·0036706	Carbon Monoxide	0·0036688
Hydrogen	0·0036613	Nitrous Oxide	0·0037195
Carbonic Acid	0·0037099	Cyanogen	0·0038767
Sulphurous Acid	0·0039028		

When the pressure was between 250 and 260 centimetres of mercury the coefficients found for air, hydrogen, and carbonic acid were 0·0036944, 0·0036616, and 0·0038455 respectively.

In the case of sulphurous acid great difficulty was always experienced in thoroughly drying the gas, and it consequently had to be allowed to enter the bulb very slowly, and so remain a long time in the drying tubes.[2] The coefficient of this gas (or of any other), near its condensing point, increases with the pressure. Thus at 760 mm. the coefficient of SO_2 was 0·003902, and at 980 mm. it was 0·003980.

Within certain limits, however, all gases may be regarded as expanding equally, that is, all gases sufficiently far removed from their condensing points approximately obey the law of Charles.

[1] Magnus, *Ann. de Chimie et de Physique*, 3e, tom. iv. p. 334, 1842.

[2] With any such gas all air should be carefully swept out of the drying tubes before filling the bulb.

114. The Pressure Coefficient.—The so-called dilatation of a gas at constant volume, or, more properly speaking, its coefficient of increase of pressure, has been studied by Rudberg, Magnus, and Regnault. The apparatus employed by all was almost exactly the same, the original apparatus adopted by Rudberg being slightly improved and perfected by the others. In its ordinary form it constitutes a constant volume air thermometer (Fig. 17). The bulb is dried and filled with dry gas as already described, and the mercury is adjusted so that its surface stands at a fixed mark a on the manometer arm. This mark was placed by Regnault on the wide part of the tube, and not on the capillary arm. He states that he could never obtain consistent results when the fixed mark was on the capillary connecting tube.

Let us suppose that the bulb is placed in ice and filled with air when the pressure of the atmosphere is H, and the difference of level in the arms of the manometer h. When it is immersed in steam let the difference of level in the two arms of the manometer be h', and the barometric height H′. The pressure of the gas in the bulb is now $\mathrm{H}'+h'$, and its temperature is $\theta°$ C., which is approximately 100° C., the difference being determined by the deviation of H′ from the standard height 760 mm. As before, if V_0 denotes the zero volume of the bulb, and v_1 the volume of the stem up to the fixed mark, the equation for α will be

$$\left(\mathrm{V}_0+\frac{v_1}{1+\alpha\theta_1}\right)(\mathrm{H}+h)=\left[\frac{\mathrm{V}_0(1+g\theta)}{1+\alpha\theta}+\frac{v_1}{1+\alpha\theta_1}\right](\mathrm{H}'+h').$$

Since v_1/V_0 is small, θ_1 may be supposed equal to θ, and we have Regnault's formula

$$1+\alpha\theta=\frac{(1+g\theta)(\mathrm{H}'+h')}{\mathrm{H}+h-\dfrac{v_1(\mathrm{H}'+h'-\mathrm{H}-h)}{\mathrm{V}_0(1+\alpha\theta_1)}}.$$

The second term in the denominator being small, an approximate value of α may be employed in it, and the calculation proceeded with by the method of successive approximations. The mean of three series of experiments by this method gave

$$\alpha=0\cdot0036679.$$

By varying the initial pressure, that is the height h, the effect of pressure may be examined. The following table is taken from Regnault's second memoir:[1]—

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. v. p. 66, 1842.

PRESSURE COEFFICIENT FOR AIR

Pressure at Zero.	Pressure at 100°.	α
109·72 mm.	149·31 mm.	0·0036482
174·36	237·17	0·0036513
266·06	395·07	0·0036542
374·67	510·35	0·0036587
375·23	510·97	0·0036572
760·00	..	0·0036650
1678·40	2286·09	0·0036760
1692·53	2306·23	0·0036800
2144·18	2924·04	0·0036894
3655·56	4992·09	0·0037091

From this table it appears that α increases gradually for air as the pressure becomes greater. This indicates that there is a small deviation from Boyle's law, which becomes more and more marked as the pressure becomes more elevated. In the case of carbonic acid this deviation is much more distinct, as shown by the following table :—

CARBONIC ACID

Pressure at Zero.	Pressure at 100°.	α.
758·47 mm.	1034·54 mm.	0·0036856
901·09	1230·37	0·0036943
1742·73	2387·72	0·0037523
3589·07	4759·03	0·0038598

115. Method of Variable Pressure and Volume.—A method in which neither the volume nor the pressure remained constant throughout the experiment was also employed by Regnault. This method is based on the assumption that the gas obeys Boyle's law, and was devised by Dulong and Petit for their experiments on the comparison of the air and mercury thermometers. It was also employed by Rudberg to determine the expansion of air. The bulbs used by Rudberg were spherical and small, containing only 150 to 200 grammes of mercury. Regnault employed much larger bulbs, which contained 800 to 1000 grammes of mercury, and were cylindrical, so as to avoid errors due to refraction in observing the level of the mercury surface through the glass. The first operation was to fill the flask with dry air at the boiling point. For this purpose it was immersed in the steam of boiling water, and connected with drying tubes and an air

pump, as shown in Fig. 41, so that it could be exhausted and dry air admitted several times. The bulb having been thoroughly desiccated and filled with dry air was allowed to remain in the steam for about half an hour. The drying tubes were then removed and the tip of the stem sealed up, the height H of the barometer being noted at the same time. The flask now contains air at a pressure H and temperature $\theta°$ which is approximately 100° C.

The second operation consists in placing the flask as shown in Fig. 42, with its stem dipping under the surface of a basin of mercury and its bulb surrounded by melting ice. In this position the tip of the stem is broken with iron pincers, and the mercury rises in the tube and partly fills the bulb. While the mercury is rising, the bulb may be gently tapped to facilitate the passage through the stem and prevent a false equilibrium occurring through the sticking of the mercury

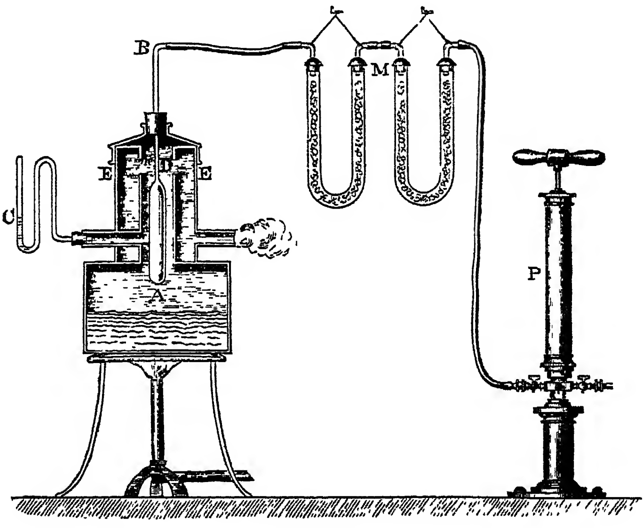


Fig. 41.

to the walls of the tube. After standing thus for an hour or more with the bulb surrounded by broken ice, the height h of the level of the mercury in the bulb, over that in the cistern, is measured by means of a cathetometer. If H′ be the height of the barometer the pressure of the air in the bulb is now $H' - h$, and its mass is the same as before. It now remains to determine its volume. For this purpose a small metal cap containing soft wax is slipped over the tip of the stem so as to close it, that the bulb and the mercury it contains may be weighed. When this weighing is effected, the instrument is completely filled with

mercury at zero and weighed again. The difference of weight gives the volume previously occupied in the bulb by the air at zero. Hence if W_0 be the weight of mercury that fills the bulb at zero, and w the weight of the mercury that ascended into it from the bath, we have

$$W_0(1+g\theta)H=(W_0-w)(1+a\theta)(H'-h),$$

or

$$1+a\theta=\frac{W_0(1+g\theta)H}{(W_0-w)(H'-h)}.$$

The coefficient deduced by Regnault as the mean result of his experiments by this method was 0·0036623, the extreme numbers being 0·0036689 and 0·0036549. His mean result is thus somewhat greater than that deduced by Rudberg; and Regnault attributes this to a source of error arising in this form of experiment and not noticed by Rudberg. This occurs in the drawing in of small bubbles of air with the mercury as the latter rises into the bulb in the second part of the experiment, and the errors arising from this source will be more marked the smaller the bulb. This aspiration, in Regnault's opinion, arises from the fact that the mercury does not wet the glass stem, and a film of air enclosed between the mercury and glass is drawn in with the mercury as it rushes up the stem after the tip is broken off.

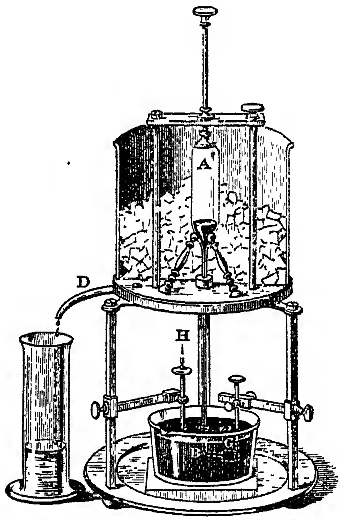


Fig. 42.

In order to avoid this, Regnault encircled the stem with small brass rings which amalgamated and made perfect contact with the mercury. He also covered the surface of the mercury with a layer of sulphuric acid, which was removed before the measurement of the height h.

Regnault conducted a further series of experiments with a modified form of apparatus. In these investigations the stem of the air-flask was made long, so that when it was opened under mercury the mercury rose to a considerable height in the stem, but did not enter the bulb. In this case h is large, and the pressure $H'-h$ of the gas enclosed is small, but its volume is nearly the same throughout the whole investigation, so that the apparatus is practically a form of constant volume air thermometer. The coefficient found by this

method was sensibly equal to that obtained by the foregoing, being 0·0036633.

The general conclusions at which Regnault arrived after his elaborate investigations were—

(1) That Gay-Lussac's coefficient, 0·00375, was too high, and that Rudberg's, 0·003645, was too low, and should be replaced by the number 0·003665.

(2) That all gases do not possess exactly the same coefficient of expansion, and that for the same gas the coefficient at constant volume differs somewhat from that under constant pressure.

(3) That the coefficient of expansion of all the gases examined (except hydrogen) increased with the density or initial pressure of the gas.

(4) That the coefficients of the several gases approach equality as the pressure of the gas decreases—that is, when the gas is taken in a highly rarefied condition.

These conclusions imply that all gases do not obey Boyle's law with the same degree of accuracy, but that when they are taken at low pressures and high temperatures, or in a highly rarefied state, their obedience to the law becomes more and more exact.[1]

[1] The mean coefficient found by Balfour Stewart (*Phil. Trans.*, 1863, p. 425) was 0·0036728. The method employed was similar to that adopted by Rudberg and used by Regnault, but abandoned for the form of apparatus in Fig. 17. The manometer tubes dipped into a closed reservoir of mercury furnished with a screw plunger, by means of which the mercury could be forced into the tubes and the level kept at the fixed mark.

The following numerical coefficients were obtained by Regnault for his various gas thermometers :—

Air thermometer normal	$272·85=(\,003665)^{-1}$
440 mm. pressure ,,	$272·98=(·0036632)^{-1}$
1490 mm. pressure ,,	$272·70=(·003667)^{-1}$
CO_2 at 464 mm.	$271·59=(·003682)^{-1}$
,, ,, 741 mm.	$270·64=(·003695)^{-1}$
SO_2 at 588 mm.	$263·\,6=(·003794)^{-1}$
,, ,, 751 mm.	$261·\,4=(·003825)^{-1}$

In the case of hydrogen, Regnault states that the coefficient used was $(·003652)^{-1}=273·82$. This, as Lord Kelvin points out, must be a mistake, as the coefficient of dilatation of hydrogen was found to be ·0036678 at constant volume, and ·0036613 at constant pressure (*Relation des Exp.*, tom. i. pp. 78, 80, 91, 115, 116), and he nowhere finds any smaller value than ·003661.

SECTION IV

DILATATION OF CRYSTALS

116. Three Principal Dilatations.—In the case of isotropic substances, the dilatation, like the other physical properties, is the same in all directions, but in crystals the expansion in any direction depends on the relation of that direction to three mutually rectangular axes, called the principal axes of dilatation, which are not necessarily the same as the axes of symmetry or crystallographic axes. Thus, in general, crystals expand differently in different directions; and some, while expanding with rise of temperature in one direction, contract in the perpendicular direction. For this reason a portion of a crystalline substance which is spherical at one temperature will not be spherical at any other, and a cubical portion at one temperature will not remain cubical when the temperature changes.

If small bars be cut from a crystal parallel to the dilatation axes, their coefficients of linear expansion will differ. The linear expansion of a bar cut parallel to one axis will be λ_1, that cut parallel to another λ_2, and that parallel to the third λ_3. It follows, therefore, that if a cube of side l_0 at zero be cut from a crystal with its edges parallel to the dilatation axes of the crystal, its edges at any other temperature $\theta°$ will be

$$l_0(1+\lambda_1\theta), \quad l_0(1+\lambda_2\theta), \quad l_0(1+\lambda_3\theta).$$

Hence its volume will be

$$V=l_0^3(1+\lambda_1\theta)(1+\lambda_2\theta)(1+\lambda_3\theta),$$

or

$$V=V_0(1+\lambda_1\theta)(1+\lambda_2\theta)(1+\lambda_3\theta).$$

The coefficient of cubical dilatation is therefore

$$\alpha=\frac{V-V_0}{V_0\theta}=\lambda_1+\lambda_2+\lambda_3,$$

neglecting the products $\lambda_1 \lambda_2$, etc.

In the case of amorphous solids and crystals of the cubic system

$\lambda_1=\lambda_2=\lambda_3$, and the cubical dilatation is three times the linear expansion.

In crystals belonging to the rhombic system there is an axis of crystalline symmetry, perpendicular to which the physical properties are alike in all directions. If λ_1 be linear expansion parallel to this axis, then the other two principal elongations are equal, or $\lambda_3=\lambda_2$; therefore for this system there are only two principal dilatations, and the cubical dilatation is

$$\alpha=\lambda_1+2\lambda_2.$$

117. Change of the Dihedral Angles of Crystals.—One of the most noticeable effects of crystalline expansion is the change of the dihedral angles, that is the angles between the plane faces of the crystal, with change of temperature. Thus if ABCD (Fig. 43) be the cross section of a square prism of a crystalline substance, cut so that the diagonals AC and BD of the section are parallel to two of the principal axes; then, when the temperature rises, AC and BD become elongated by different amounts, and the cross section of the prism remains no longer square, but changes into a rhombus A′B′C′D′. The angles at A and C become acute, while those at B and D become obtuse. If two such prisms be cemented together with two edges in contact, whose angles become more obtuse by heating, then if when cool the two upper faces form one continuous plane, they will be inclined as shown in Fig. 44 when heated. Exceedingly small inequalities of expansion in different directions may be

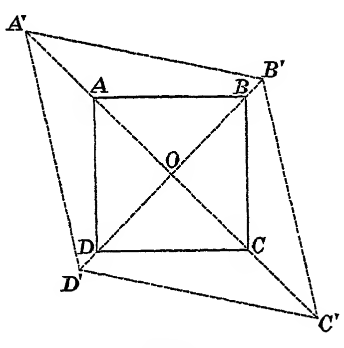


Fig. 43.

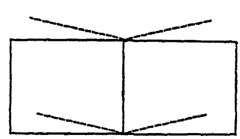


Fig. 44.

detected in this manner by observing through a telescope the image of a distant object formed by reflection at the polished surfaces of the combined prisms.

Mitscherlich seems to have been the first to notice that crystals expanded differently in different directions, and his method of

observation[1] consisted in determining the variations of the dihedral angles of crystals with change of temperature. The angles between the plane faces of a crystal may be measured with great accuracy by optical instruments, such as the reflecting goniometer, and such measurements are in general more exact for these investigations than any direct measurement of length. The method, however, does not give the absolute dilatation, but only the difference of the elongations in the direction of the diagonals of the prism. Denoting these by λ_1 and λ_2 we have

$$\tan \mathrm{OB'A'} = \frac{1+\lambda_1\theta}{1+\lambda_2\theta} = 1 + (\lambda_1 - \lambda_2)\theta,$$

and OB′A′ is half the measured angle of the rhombus.

Another relation between the principal elongations is obtained by measuring the cubical dilatation. This gives the sum $\lambda_1 + \lambda_2 + \lambda_3$, and may be determined by means of the weight thermometer. If the substance belongs to the rhombic system we have $\lambda_2 = \lambda_3$, and these two measurements determine the elongations λ_1 and λ_2. Mitscherlich[2] and Dulong determined the cubical dilatation of a number of crystals by the method of the weight thermometer. Any two other observations combined with this determine the three quantities λ_1, λ_2, λ_3. A series of experiments on this subject was executed by Pfaff,[3] who found that Iceland spar and beryl contract transversely with rise of temperature.

118. Linear Dilatation in any Direction.—So far we have only considered the linear dilatations parallel to the principal axes of dilatation. The linear dilatation in any other direction may be simply expressed in terms of the quantities λ_1, λ_2, λ_3, and the angles α, β, γ, which the direction makes with the axes of reference.

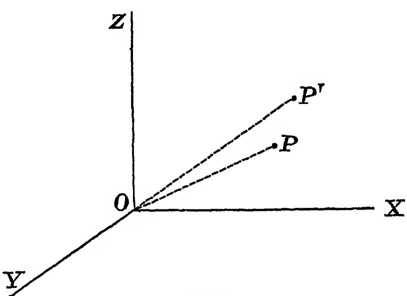


FIG. 45.

Let the axes of reference OX, OY, OZ (Fig. 45) be taken parallel to the three principal axes of dilatation, and let the coordinates of any point P be x, y, z at the temperature zero. The distance of P from the origin is given by the equation

$$r^2 = x^2 + y^2 + z^2.$$

[1] Mitscherlich, *Ann. de Chimie et de Physique*, 2e, tom. xxv. p. 108, 1824; tom. xxxii. p. 111, 1826.

[2] Mitscherlich, *Pogg. Ann.* vol. xli.

[3] Pfaff, *Pogg. Ann.* vol. civ. cvii., 1859.

At any other temperature θ, P will occupy a position P′, the co-ordinates of which are

$$(1+\lambda_1\theta)x, \quad (1+\lambda_2\theta)y, \quad (1+\lambda_3\theta)z,$$

and the distance r' of P′ from the origin will be

$$r'^2=(1+\lambda_1\theta)^2x^2+(1+\lambda_2\theta)^2y^2+(1+\lambda_3\theta)^2z^2,$$

or approximately

$$r'^2=r^2+2\theta(\lambda_1x^2+\lambda_2y^2+\lambda_3z^2).$$

Now by the expansion the line OP becomes the line OP′, and therefore the linear dilatation in the direction OP, that is of a bar cut parallel to OP, is

$$\lambda=\frac{r'-r}{r\theta}.$$

But since $r+r'$ is very nearly equal to $2r$, we have

$$\lambda=\frac{r'-r}{r\theta}=\frac{r'^2-r^2}{2r^2\theta}=\frac{\lambda_1x^2+\lambda_2y^2+\lambda_3z^2}{r^2},$$

or

$$\lambda=\lambda_1\cos^2\alpha+\lambda_2\cos^2\beta+\lambda_3\cos^2\gamma,$$

where α, β, γ are the angles which OP makes with the axes of reference. Thus by three measurements of λ made in any three known directions, the quantities λ_1, λ_2, λ_3 can be calculated.

Cor. 1. The linear dilatations, λ', λ'', λ''', in any three mutually rectangular directions are such that their sum, $\lambda'+\lambda''+\lambda'''$, is constant, and equal to the cubical dilatation.

Cor. 2. In a direction equally inclined to the axes we have

$$\cos^2\lambda=\cos^2\mu=\cos^2\nu=\tfrac{1}{3},$$

and a single measurement of λ in this direction gives the cubical dilatation $\alpha=3\lambda$.

Cor. 3. There are an infinite number of directions parallel to the generators of the cone (when real)

$$\lambda_1x^2+\lambda_2y^2+\lambda_3z^2=0,$$

along which there is neither contraction nor expansion.

This property is possessed by certain classes of marble. Brewster suggested the use of a rod of marble cut in this direction as a pendulum of invariable length.

119. Fizeau's Optical Method.—An optical method depending on the colours of thin plates was designed by M. Fizeau[1] for the measurement of the dilatations of crystals and other substances, which can

[1] Fizeau, *Ann. de Chimie et de Physique*, 4e, tom. ii., 1864; and tom. viii. p. 335, 1866.

only be obtained in small fragments. The substance to be examined was cut into a plate with parallel faces, and from 1 to 10 mm. thick. This plate, P (Fig. 46), rested on a plane metal disc, AB, which was supported on three adjustable screws passing through it near the circumference. On the upper extremities of these screws rested a glass plate, CD, which could be brought very close to the crystalline plate by adjusting the supporting screws. A beam of light fell perpendicularly on the glass plate, and passing through was partially reflected at the upper surface of the crystal. When the air film between the glass plate and the crystal is sufficiently thin, coloured fringes are produced, which vary with the thickness of the film.[1] When the temperature rises the thickness of the crystalline plate changes, as well as the lengths of the screws supporting the glass plate. Hence the thickness of the air film between the glass plate and the crystal will change by an amount equal to the difference of the expansion of the crystal, and the expansion of the length of screw between the metal and glass plate. But when the thickness of the air film changes the fringes are displaced, and from observation of this displacement the change of thickness can be calculated, and hence the expansion of the crystal deduced.

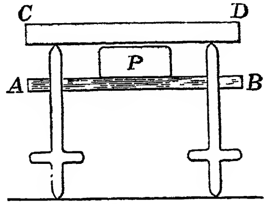


Fig. 46.

By this means exceedingly small changes of thickness can be observed. Thus in order to displace Newton's rings through the width of a bright or dark band, a change of thickness of the air film of one-fourth of a wave-length of light is sufficient. For yellow light the wave-length is about 0·00059 mm., and a displacement of one-fifth of a band width can be easily observed, so that a change of thickness of the air film of less than $\frac{1}{30000}$ of a millimetre can be detected. Thus a plate of rock crystal 5 mm. thick dilates by about $\frac{1}{370}$ of a millimetre, when the temperature changes from 10° to 50° C., and this would give a displacement through nine entire fringes.

In order to observe the displacement of the fringes, lines were ruled on the glass, and the position of the fringes with respect to them could be observed. The light thus acts the part of a most delicate micrometer, the only condition necessary being an exact knowledge of the wave-length of the light employed.

[1] If the surfaces were accurately plane and parallel, a beam of parallel light falling on the apparatus would not produce fringes, but only a certain colour over the film; in practice, however, perfectly plane surfaces are never realised, and fringes of some sort are always presented.

The whole apparatus could be placed in an oven, and maintained at any desired temperature. The expansion of the screws was determined by making observations without the plate of crystal between. The earlier forms of the apparatus were made of steel, but in the later an alloy of platinum with $\frac{1}{10}$ of iridium was used, on account of its greater stability in all respects. If the crystalline plate is transparent its lower face should be blackened to prevent reflection at that face, and thus secure greater distinctness of the fringes.

Fizeau worked with three equidistant temperatures—10°, 40°, 70° C. Writing λ and α in the forms

$$\lambda = a + b(\theta - 40°)$$
$$\alpha = c + d(\theta - 40°)$$

he obtained for emerald, which belongs to the hexagonal system,

$$\lambda_1 = -0{\cdot}00000106 + 0{\cdot}0000000114(\theta - 40°)$$
$$\lambda_2 = +0{\cdot}00000137 + 0{\cdot}0000000133(\theta - 40°)\ ;$$

hence

$$\alpha = \lambda_1 + 2\lambda_2 = 0{\cdot}00000168 + 0{\cdot}0000000380(\theta - 40°).$$

Thus within the range observed λ_1 is negative, and emerald contracts along this axis as the temperature increases. It also appears that the cubical dilatation α is positive above the temperature $-4°{\cdot}2$ C. and negative below it, and consequently at this temperature emerald appears to present a maximum density as in the case of water at 4° C. For diamond, which belongs to the cubic system,

$$\alpha = 3\lambda = 0{\cdot}00000354 + 0000000432(\theta - 40°),$$

and a maximum density is presented at the temperature $-42°{\cdot}3$ C.

In the case of oxide of copper (cubic system)

$$\alpha = 3\lambda = 0{\cdot}00000279 + 0{\cdot}000000063(\theta - 40°),$$

so that a maximum density is presented at the temperature $-4°{\cdot}3$.

Iodide of silver exhibited a negative coefficient of dilatation throughout the whole range of temperature employed, $-10°$ to $+70°$. Within these limits it contracts when the temperature rises, and expands again on cooling. The formula for α, however, points to a minimum density at the temperature $-60°$ C.

CHAPTER IV

CALORIMETRY

SECTION I

INTRODUCTORY

120. The General Methods of Calorimetry.—The measurement of quantities of heat by any method has been styled calorimetry, and there is perhaps no department of scientific research in which experimental skill is more constantly and severely tested. In such measurements we require no knowledge of the ultimate nature of heat, whether it be a fluid or an action, either at a distance or propagated through a medium; the estimation is simply based on the measurement of some effect attributed to heat. For this reason the term "quantity of heat," although introduced at a time when heat was supposed to be a fluid, may still be retained with a certain definiteness of meaning, independent of any theory, just as quantities of light and quantities of electricity are referred to with a certain amount of intelligibility without necessarily implying a complete knowledge of the ultimate nature of either.

The general methods adopted for the measurement of quantities of heat may be placed under two heads, depending on

(1) Change of State, or Latent Heat Calorimetry.
(2) Change of Temperature, or Thermometric Calorimetry.

The first group embraces those methods which are founded on the fusion of solids, or the condensation of vapours, or on the reverse operations, and includes the ice and steam calorimeters. This method, since it depends on the latent heat of fusion or evaporation, requires the use of fixed temperatures only, and does not necessitate the employment of a thermometer. The second group, on the other hand, embraces those methods in which the temperature is variable, and the measurement essentially depends on changes of temperature. In this system the estimation is reduced to the observation of temperatures, and the thermometer becomes the instrument of prime importance.

For this reason it has been termed thermometric calorimetry. It embraces the celebrated method of mixtures so extensively employed by Regnault, and the method of cooling which was perfected by Dulong and Petit.

121. Units and Quantities of Heat.—The employment of these two general methods in calorimetry has led to the adoption of two different units of heat. In the method of latent heat the substance usually employed was ice, and quantities of heat were measured by the quantities of ice which they melted. The unit of heat in this system was naturally the quantity of heat required to convert unit weight of ice (at the melting point) into ice-cold water. In the second system, quantities of heat were measured by the quantities of water which they raised through some definite range of temperature, and the unit chosen in this system was that which is now generally adopted, namely the quantity of heat required to raise unit weight of pure water one degree in temperature. When the unit of weight is taken as one gramme, and the degree centigrade as the interval of temperature, the unit of heat may be termed a *calorie*, and it is in terms of this unit that quantities of heat are now chiefly expressed. The first unit is about eighty times as large as this, or the quantity of heat required to liquefy any mass of ice without raising its temperature would raise the temperature of a mass of water eighty times as great one degree centigrade. It is in this sense that the latent heat of ice is said to be 80.

A third method of obtaining equal quantities of heat, or any multiple of a quantity, is by means of a steady flame, or any body maintained in a state of steady incandescence, or by a wire kept at a steady temperature by means of an electric current. Thus a certain quantity of heat will be developed by the combustion[1] of a gramme

[1] If equal quantities of heat be given to equal masses of two substances their specific heats will be inversely as the corresponding changes of temperature. The electric method was employed by Joule, and the combustion method was used by Black, but soon abandoned on account of its many sources of inaccuracy. It was, however, more recently used by Thomsen (*Journal de Physique*, tom. i. p. 35) with greater success. (Hirn's method is mentioned below, p. 263.) Thomsen operated with about a litre of liquid placed in a calorimeter, which was heated centrally by the combustion of a certain mass of hydrogen, which was the same in all experiments. He commenced each experiment with the temperature of the calorimeter as much below that of the air as its final temperature was above it. Marignac employed a large-bulbed thermometer filled with water as heater (Hirn's method), and eliminated the radiation correction by varying the mass of liquid in the calorimeter, so that the final temperature was the same in all experiments, and the same as that attained by a known quantity of water in another experiment. The quantity of heat supplied being the same in all cases, it followed that the specific heats of the various substances were inversely as the masses. For if Q be the quantity of heat supplied in

of hydrogen in oxygen, and n times as much will be produced by the combustion of n grammes under the same conditions. This method, however, suffers from many imperfections, and is difficult to work with, besides requiring for accuracy many precautions and auxiliary experiments.

The convenience of the calorie arises partly from the comparative facility with which pure water can be procured, and from the fact that sensibly the same quantity of heat is required to raise the temperature of a given mass of water one degree at any temperature between the freezing and boiling points. This property of water must be tested by mixing equal masses, or known masses, of water at different temperatures, and observing the resulting temperature of the mixture. If equal masses at temperatures θ and θ' be mixed, and if the same quantity of heat is required to raise the temperature of each one degree at all parts of the scale, then the temperature of the mixture will be the arithmetic mean of θ and θ', that is $\frac{1}{2}(\theta + \theta')$. If the temperature of the mixture differs from this when all corrections are allowed for, it is to be concluded that the quantity of heat required to raise the temperature of the mass one degree is not the same at all temperatures, or, in other words, the thermal capacity (Art. 23) of the mass varies with the temperature.

Specific heat of water.

If the unit of heat is definitely chosen as the quantity of heat which will raise the temperature of one gramme of water from 4° to 5° C., then a quantity Q of heat is that which will raise the temperature of Q grammes of water through the same interval, and not the quantity which will raise the temperature of one gramme of water Q° C. The latter quantity will be the same as the former only if water happens to possess the same thermal capacity at all temperatures; and since water is the standard substance, this point can be decided only by mixing quantities of water at different temperatures, or by comparison with some standard depending on the same process. The most recent investigations on this subject show that the thermal capacity of water is not exactly constant, but diminishes slightly from zero to about 20° C., and then gradually increases again. It thus exhibits a minimum value at about 20° C. The variation is, however,

each case by the heater, R the quantity lost by radiation, and θ the change of temperature, we have for masses m and m'—

$$Q - R = mS\theta = m's'\theta,$$

or

$$\frac{s}{s'} = \frac{m'}{m}.$$

The results obtained by Thomsen and Marignac by these methods agree remarkably well.

very small, and consequently we shall hereafter speak generally of water as if its thermal capacity remained constant at all ordinary temperatures, and with this license we can say that the quantity of heat required to raise the temperature of m grammes of water from θ to θ' is

$$Q = m(\theta' - \theta),$$

and this assumes that the specific heat of water is unity between the temperatures θ and θ'.

In most cases in which quantities of heat are measured it is assumed that in the interchange of heat between two bodies the quantity of heat which one loses is the same as the quantity which the other gains. No third body is supposed to take part in the operation, and heat is supposed not to be developed or destroyed by chemical or other actions between the bodies. Thus if two bodies A and B at different temperatures are simultaneously immersed in a known weight of water, they raise its temperature by a certain amount, and it is found that the final temperature of the water is the same if A and B are first brought into contact, so as to come to the same temperature before immersion. In the first case the heat is directly transferred from A and B to the water; in the second case some of the heat passes from A (supposed the warmer) to B before immersion, and is afterwards transferred to the water; finally, however, the whole quantity received by the water is the same in the two cases.

The final admission is, that if a body absorbs a quantity Q of heat in changing its temperature from θ to θ' under given conditions, then during the reverse process, during the passage of the body back again from θ' to θ under exactly the same conditions, the same quantity Q of heat will be evolved by the same body. If this were not so, a body, when alternately heated and cooled under the same conditions, would act perpetually as a source or sink of heat, and the principle of the conservation of energy would be violated. To the calorists, who regarded heat as an indestructible fluid, this equality appeared self-evident, and was accordingly tacitly assumed. From the point of view of the dynamical theory, however, heat may be called into existence by mechanical actions, and it is not the quantity of heat, but the quantity of energy in a system that is conserved. Hence it does not necessarily follow that a body will absorb the same quantity of heat in passing from one state A to another B as it will evolve in returning from B to A. If, however, it passes back again from B to A in the reverse order, through exactly the same series of states and under exactly the same conditions as during its passage from A to B, the

quantity absorbed will be equal to that evolved. The consideration of such transformations will be more fully entered into in Chap. VIII.

122. Specific Heat.—The specific heat of a substance has been already defined (Art. 23) as its thermal capacity per unit mass, or, in other words, the ratio of the quantity of heat required to raise the temperature of a given weight of it by a given amount to the quantity necessary to raise the temperature of an equal weight of water by the same amount. Now, since the unit of heat is taken to be the quantity which raises the temperature of one gramme of water 1° C., it follows that the quantity which will raise the temperature of a gramme from θ to θ' will be simply $\theta' - \theta$; and consequently, if a quantity Q raises the temperature of one gramme of any substance from θ to θ', the specific heat of the substance will be, by definition,

$$s = \frac{Q}{\theta' - \theta}.$$

In this case s is the *mean* specific heat of the substance between θ and θ'; and if we wish to speak of the specific heat of a substance at any temperature θ, we must take θ' infinitely near θ. Denoting the infinitesimal difference $\theta' - \theta$ by $d\theta$, and the corresponding quantity of heat by dQ, we have

$$s = \frac{dQ}{d\theta}.$$

That is, the specific heat of any substance at the temperature θ is the ratio of the quantity of heat dQ required to change the temperature of unit mass by an amount $d\theta$ to the change of temperature $d\theta$.

Case of gases.

In general, when the specific heat of any substance is spoken of, the conditions under which the change of temperature occurs should be distinctly specified, for the temperature of a body may be varied by mechanical actions alone. Thus, the temperature of a gas may be raised by compression, so that here we have dQ equal to zero, while $d\theta$ does not vanish, and the specific heat would appear to be zero. On the other hand, a finite quantity of heat may be given to a gas, while at the same time it is allowed to expand so as to remain at a fixed temperature. In this case $d\theta$ vanishes and dQ does not, so that the specific heat is infinite. The expansion of the gas might also be permitted to proceed so far that, although heat is actually given to it, yet its temperature will be lowered, that is, $d\theta$ will be negative, and the specific heat may thus have any negative value. It thus appears that the specific heat of a gas may have any value between $+\infty$ and $-\infty$, according to the conditions under which the heat is communicated. To speak with definiteness, therefore, of the specific heat of a gas, it is

necessary to assign the conditions under which the temperature changes. For example, we may speak of the specific heat under constant pressure, or at constant volume.

Solids and liquids.

In the case of liquids and solids, the compressibility is so small that under the conditions of all ordinary experiments changes of volume need not be taken into account, and we are not complicated with a multiplicity of specific heats, as in the case of a gas. Each liquid and solid may therefore be said to have a definite specific heat at each temperature; but the specific heat of each substance is not the same at all temperatures. As a general rule, it may be said that the specific heat of a solid or liquid increases with the temperature.

Setting out with a solid, say at zero, the relation between the quantity of heat supplied to it, and the corresponding elevation of temperature, is roughly shown by Fig. 47. Measuring temperature parallel to the axis of OX, and quantities of heat parallel to OY, the

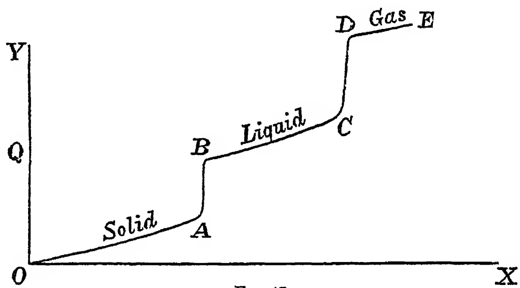


Fig. 47.

ordinate of any point on the curve OA represents the quantity of heat given to the solid in raising its temperature from zero to that represented by the corresponding abscissa. If the specific heat were constant, OA would be a right line, and the tangent of the angle which it makes with OX would represent the specific heat. If, however, the specific heat increases with the temperature, OA will be convex towards the axis of x, and the trigonometrical tangent of the angle which the tangent to OA at any point makes with OX will be the specific heat $dQ/d\theta$ at the temperature corresponding to that point.

At the point A, fusion is supposed to begin, and a certain quantity of heat (the latent heat of fusion), represented by the vertical line AB, is communicated to the body without any change of temperature. At B liquefaction is complete, and the curve BC applies to the liquid in the same manner as OA does to the solid. Similarly, CD represents the latent heat of vaporisation, and DE applies to the vapour under some definite conditions of pressure and volume.

In the foregoing, the comparison has been made between equal masses of different substances, and this may be therefore referred to as the *mass* specific heat. If the comparison had been made between equal volumes, that is, if the specific heat had been taken to be the quantity of heat required to raise the temperature of unit volume of the substance 1° C., this might be termed the *volume* specific heat. The relation between the two is very simple. For if a quantity Q of heat raises the temperature of a mass m through $\theta°$, then Mass and volume.

$$Q = ms\theta,$$

and if the same quantity raises a volume v through θ, we have

$$Q = vs'\theta,$$

where s' is the volume specific heat and v is the volume of the mass m. Hence

$$s' = s\frac{m}{v} = s\rho,$$

where ρ is the density of the substance referred to water.

123. Absolute Specific Heat.—The ordinary specific heat of a substance has been defined as the quantity of heat required to increase the temperature of unit mass of the substance 1° C., under given conditions. In general, this quantity of heat will be expended in several ways. If the body expands, work will be done against the external pressure. This is termed the external work, and an equivalent quantity of heat will be spent in performing it. During the dilatation the molecules will be separated further apart, and work will be done against their mutual attraction. This may be termed the internal work. The remainder of the heat will be spent in increasing the energy of motion of the molecules; and this may be divided into three parts—the energy of translation, the energy of rotation, and the energy of vibration. These three parts may be related to each other in any way, but it is generally considered in the dynamical theory that they are proportional to each other, so that if E denotes the mean energy of translation of a molecule, the mean energy of rotation will be aE, and the mean energy of vibration bE. Thus, when one of these vanishes, each of the others vanishes also, and the molecule comes to rest (see Art. 57).

Now, if heat be due to waves in the ether, it will be caused by the vibrations of the molecules, and consequently it will be the change of the energy of vibration that will determine the change of temperature. For this reason the quantity of heat (or work) spent in changing the mean energy of vibration of the molecules per unit mass

while the temperature increases 1° C., is termed the absolute specific heat of the substance. It is obviously less than the ordinary specific heat by the quantity of heat spent, during the same change of temperature, in doing the external and internal work, and in increasing the mean energies of translation and rotation of the molecules. At present, however, we have little definite knowledge as to the mode of partition of the energy between the different forms of motion, or of the amount of internal work done against molecular attraction, so that the term absolute specific heat remains so far only as a name.

SECTION II

THE METHOD OF MELTING ICE

124. Black's Ice Calorimeter.—The earliest form of ice calorimeter was that devised by Black. It consisted merely of a block of pure ice, free from bubbles, in which a cavity (Fig. 48) was hollowed out. The mouth of this cavity was covered over by another slab of ice, so that a chamber was obtained, which was enclosed on all sides by ice at the melting point.

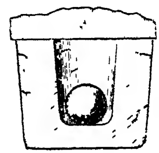


Fig. 48.

In making an experiment, a known weight of the substance under examination was heated to some definite temperature, say the boiling point of water. The ice chamber was then carefully dried with a sponge or blotting-paper, so that no water was left adhering to its walls. The heated body was then quickly placed within, and the upper slab laid over the mouth of the chamber. The body quickly fell to the temperature of melting ice, and a certain quantity of ice was liquefied. This quantity was estimated by wiping dry the whole interior of the cavity, as well as the surface of the body, with a cold sponge (or blotting-paper), which had been previously weighed. The increase of weight gave the quantity of water absorbed—that is, the mass of ice melted.

If the unit of heat be taken as that which melts unit mass of ice at zero, then the quantity of heat given out by the body in this experiment will be numerically the same as the mass of ice melted, that is w, suppose. But if the initial temperature of the body be θ', its final temperature $0°$, its mass m, and its specific heat s, the quantity of heat given out will be $ms\theta$. Consequently we have the equation

$$ms\theta = w,$$

where m and w are expressed in the same units. Expressed in ordinary units of heat (calories) the equation would be

$$ms\theta = \mathrm{L}w,$$

where L is the latent heat of ice, or the quantity, expressed in calories, which will melt a gramme of ice (= 79·25). If the value of L, which may be called the constant of the calorimeter, be not known, an experiment will be necessary in order to determine it. This may be effected by introducing into the ice-chamber a weighed quantity of water at a known temperature, and finding as before the quantity of ice melted.

The chief objection to this apparatus is the difficulty of procuring large pieces of ice of sufficient purity.

125. Lavoisier and Laplace's Ice Calorimeter.—A modified form of Black's calorimeter was devised by MM. Lavoisier and Laplace,[1] in which the necessity for large blocks of pure ice is avoided. It consists essentially of three chambers (Fig. 49) contained one within the other. The inner chamber AB contains the hot body whose specific heat is desired. This chamber is surrounded by another, and the space C between them is packed with broken ice at zero. A tube F leads from this chamber and drains off the water resulting from the melting of the ice. This water is weighed and the specific heat of the substance is estimated as before. In order to avoid heating from outside, a jacket of ice DDD surrounds the second chamber. For this purpose, the space between the second chamber and the outside walls of the instrument is filled with broken ice, and as the ice is melted in this chamber by radiation from outside, the water drips away by the tap E. When the apparatus is in proper condition for an experiment, there should be no flow from the tap F, but a constant drip from the tap E. If now a hot body is placed in the chamber A, its heat will be given out to melt the ice in C, causing a corresponding flow of water from F.

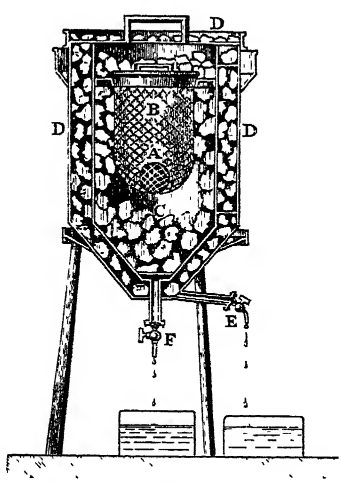


Fig. 49.
Lavoisier and Laplace's Ice Calorimeter.

This apparatus requires a large quantity of ice, and large masses of the substance under examination, and consequently a long time for the execution of an experiment, and the trifling advantage it possesses over Black's simple apparatus in not requiring the use of large blocks of pure ice is more than counterbalanced by difficulties of the gravest

[1] *Mémoires de l'Académie*, 1780 ; *Œuvres de Lavoisier*, tom. ii. p. 283.

nature in estimating the quantity of ice melted. This arises from the water adhering to the ice, and remaining in the interstices between the fragments. At the beginning of the experiment, the ice is mixed with a certain quantity of adhering water, which in all probability will be considerably different at the end of the experiment, for during the experiment the size and arrangement of some of the ice fragments will alter. Hence the quantity of water which drains off through the tap F during the experiment does not accurately represent the quantity of ice melted, nor have we any means of estimating the probable error thus introduced.

In the hands of Lavoisier and Laplace this instrument yielded fair results, but with less scientific and careful experimenters the adhesion of the water to the ice might easily lead to great inaccuracies. In order to avoid this difficulty, Sir John Herschel suggested that the water should not be drained off, but that it and the ice should be kept together, and the whole bulk measured before and after melting. The diminution of bulk would thus give the quantity of ice melted during the experiment. An ingenious method of measuring this change of volume has been devised by Bunsen[1] in his ice calorimeter, an instrument possessing many novel features of remarkable beauty and interest. It is particularly valuable for measuring small quantities of heat, and by means of it Professor Bunsen has determined the specific heats of rare metals, such as indium, which can only be obtained in small quantities. It is, however, by no means easy to work with, and the theoretical conditions which are supposed to be fulfilled are difficult to realise in practice.

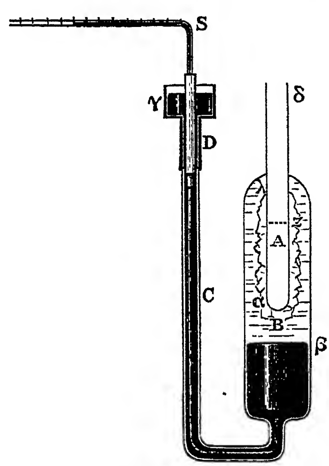


Fig. 50.

126. Bunsen's Ice Calorimeter.—As already stated, this apparatus is designed especially for the measurement of the change of volume which occurs during the liquefaction of ice. For this purpose a cylindrical test-tube A is fused into a larger cylindrical glass bulb B, as shown in Fig. 50. The bulb B is furnished with a glass stem CD, which terminates in an iron collar D. This stem is filled with pure boiled mercury, which also occupies the bulb to the level β. The

[1] *Pogg. Ann.*, vol. cxli.; *Ann. de Chimie et de Phys.*, 3e, tom. xxiii. p. 50; *Phil. Mag.*, 1871, vol. xli. p. 161.

remainder of the bulb above β is filled with pure boiled water. A calibrated narrow glass tube S, furnished with a millimetre scale, is fitted into a cork with fine sealing-wax, and then passed through the mercury in the collar D, and made fast in the mouth of the tube CD, so that it becomes filled with mercury; and by adjusting the cork in the mouth of the tube CD, the extremity of the mercury column in the scale-tube S can be placed at any convenient point. To effect this without risk to the fragile apparatus, the instrument is supported by the iron collar D in a vice.

In conducting an experiment, the first operation is to freeze some of the water in the bulb B. For this purpose the ice-producing apparatus shown in Fig. 51 was employed by Bunsen. F and G are two semi-cylindrical tin-plate vessels, which are connected by tubes with the test-tube A of the calorimeter, as shown in figure. The vessels F and G contain alcohol, and are both placed in a freezing mixture. By suction the cold alcohol can be passed to and fro from F to G through the calorimeter tube A, and by this means the water in the bulb B can be reduced to the freezing point.

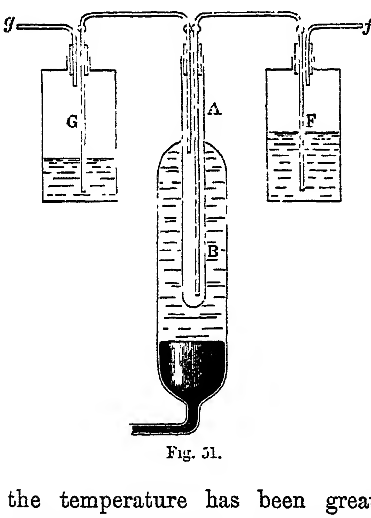


Fig. 51.

The temperature of the air-freed water in B must be reduced far below the normal freezing point before solidification sets in, while the outside of the bulb becomes covered with a coating of ice, deposited from the moisture of the atmosphere. At last, when the temperature has been greatly reduced, the formation of ice suddenly begins, and spreads in a few seconds from the bottom of the tube A to the top of the bulb B. Within these limits the bulb is filled with thin plates and needles of ice, but from the bottom of A to the level of the mercury below the water is not frozen. By continued cooling a shell of solid ice may be gradually formed around A, from 6 to 10 mm. in thickness. On account of the low temperature of the alcohol, the ice shell is much below zero, and if the instrument is now packed in snow at zero a slow progressive freezing will take place in the water for a long time. Bunsen found that in this manner about 2 grammes of water were frozen at the temperature of melting snow during the first seven hours, and that this progressive

freezing was sensible for 114 hours. After this time the whole apparatus had come to zero, and the freezing ceased.

In making an experiment, the instrument is packed in pure snow, and some pure water is placed in the tube A. The temperature of the whole apparatus is now zero, and it may be maintained in this condition for a week or more if some fresh snow is added from day to day. It is very important that the snow should be quite pure, for if it contains even traces of impurities its melting point is lowered, and a slow progressive freezing of the water in the bulb takes place.[1] It is also well to work in a room which is at a temperature not much above the freezing point, and before the instrument has assumed the constant temperature of the snow it is necessary to see that a thin layer of water is formed between the ice shell and the sides of the glass tube A, so as to avoid inequalities of pressure.

In order to interpret the indications of the instrument, a known mass of water m, at a definite temperature θ, may be introduced into the tube A. In falling to zero this gives out a quantity of heat $m\theta$, and in consequence of the melting of the ice the mercury in the tube S recedes through n divisions of the scale. This gives the relation between the quantity of heat supplied in any experiment in the tube A, and the corresponding recession of the mercury along the scale S.

In determining the specific heat of any substance, a fragment of it is heated in a steam-jacket, and the test-tube is partially filled with pure distilled water. The heated fragment is quickly immersed in it, a plug of cotton wool being placed at the bottom of A to prevent fracture. The water in A is initially at zero, and its lower strata become warmed by the hot body; but water being denser for some range above zero than at zero, the heated water remains at the bottom of the tube, and gives up its heat in melting the ice in the bulb B. If the mercury recedes through n divisions of the scale, and if q is the quantity of heat corresponding to each division, the whole heat given up by the body in cooling to zero is nq. Hence, if m be the mass of the body, its specific heat is given by the equation

$$ms\theta = nq.$$

In practice, the end of the mercury column does not remain stationary, but may vary in either direction by two or three divisions per hour. The error arising from this variation is approximately proportional to the time, and is corrected by observing the motion of the index for

[1] Professor C. V. Boys found that this effect was largely reduced when the bulb was provided with a protecting glass cover (*Phil. Mag.* vol. xxiv. p. 214, 1887).

half an hour before and half an hour after the experiment. If a variation of n_1 scale divisions occurs in a time t_1 before the experiment is commenced, and n_2 in a time t_2 after it is completed, the mean rate of variation during the experiment may be taken equal to $\frac{1}{2}\left(\frac{n_1}{t_1}+\frac{n_2}{t_2}\right)$, and this multiplied by the time of the experiment gives the whole correction to be applied to the reading arising from this cause.

The accuracy of the instrument depends essentially on the care with which all the air has been expelled from the water enclosed by the bulb B. In order to secure this, the bulb is at first about half-filled with water, and placed mouth downwards over a lamp, so that the water can be boiled and the air expelled through the tube CD. During this process the mouth of the tube CD, which has not yet been fitted with the iron collar, dips into a vessel of boiling water. When the water in the bulb has been boiled away to about one-third of its original bulk the lamp is removed, and as the instrument co[illegible] free water is siphoned over into it through the tube CD f[illegible] into which it dips. The instrument is now placed [illegible] water for the most part siphoned out of the tub[illegible] well dried by a current of dry air, and the iron with the finest sealing-wax. The final filling-i[illegible] done with a capillary glass tube, so as to avo[illegible] air bubbles on the sides of the tube[illegible]

By pressing the cork which c[illegible] the mouth of the tube CD, the placed at the same point of [illegible] experiment, and the same part [illegible] a series of investigations. Over with the same cylinder of ice, s[illegible] a week, if care be taken to re[illegible] every night and morning.

From the mode of standardis[illegible] error is introduced by an inaccur[illegible] ice. Radiation errors are also ent[illegible] snow, if the temperature of the latter exp[illegible]

By means of this apparatus the latent heat o[illegible] if the volume of each division of the scale tube b[illegible] pansion of water on solidifying at zero be also k[illegible] Bunsen found the value 80·025, while the value Person, and Hess, by other methods, were 79·4, [illegible] spectively.

SECTION III

THE METHOD OF MIXTURES

127. Preliminary Considerations.—The most prevalent method of calorimetry hitherto employed has been founded neither on the melting of ice, nor on the evaporation or condensation of a liquid, in y principle of latent heat, but on the measurement of heat

of water. This method passes mixtures,[1] and since the time of ıethod *par excellence* in the science

A_1 and A_2, of masses m_1 and m_2, mperatures θ_1 and θ_2. If A_1 and pass from one to the other, and iate between θ_1 and θ_2 will be t by A_1 will be $m_1 s_1(\theta_1 - \theta)$, and $s_2(\theta - \theta_2)$. Consequently, if the $_1$ and A_2, that is, if they neither er bodies during the period of lost by A_1 will be equal to that

$s_2(\theta - \theta_2)$.

equal to unity by definition, and by the equation

$$\frac{\vartheta - \theta_2)}{\vartheta_1 - \theta)}.$$

ıe mean specific heat of A_1 between

[redacted]at thermal equilibrium takes place between A_1 and A_2 without loss or gain of heat, that they neither give heat to nor receive heat from other bodies during the period of equal-

[1] This method was employed by Black.

isation of temperature. In practice it is impossible to secure this condition accurately, and in general there will be interchange of heat with other bodies. For this reason corrections must be applied, and special apparatus adopted, to eliminate or minimise such errors. The whole science of calorimetry consists of the invention of such apparatus and the adoption of such precautions as will lead to an accurate estimate of these corrections.

128. The Water Calorimeter.—The principal piece of apparatus necessary for the determination of specific heats by the method of mixtures is the water calorimeter. This consists of a cylindrical vessel (Fig. 52) made of very thin brass or copper or silver, and sustained within a somewhat larger and stronger vessel by non-conducting supports. The inner vessel contains a known quantity of water in which the body under investigation is placed at a known temperature, and the change of

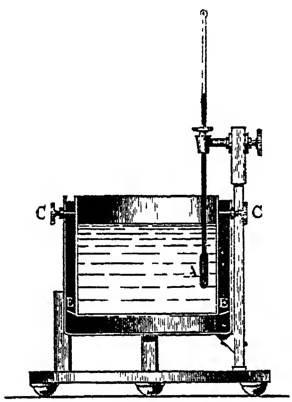


Fig. 52.

temperature of the v
of a delicate therr
it, which may be o
through a telescope.
the loss of heat by
tion during this observation the outs e of th
inside of the outer are both carefully polished
emissive power of one and the absorbing pc
greatly reduced. The inner vessel is supporte
threads EE stretched horizontally across the
tained in its place by wooden pegs CC wh
of the outer vessel near its mouth, and pr
it steady.

In every investigation it is supposed that
its equipages, such as the stirring-rod and the
the same temperature at the beginning and als of
experiment. Let us suppose that a body of mass m, at a temperature θ, and of specific heat s, is immersed in the water, and let the temperature of the water rise in consequence from θ_1 to θ_2. During this process not only the water, but also the metal of the inner vessel and the material of the thermometer and stirring-rod, have been raised from θ_1 to θ_2, and their thermal capacities must therefore be taken into account. In the case of a body of mass m_1 and specific heat s_1 the quantity of heat necessary to raise its temperature 1° C. is $m_1 s_1$, and

this is numerically the same as the mass of water which the same quantity of heat would raise 1° C. in temperature. For this reason $m_1 s_1$ is termed the *water equivalent* of the body, for it is numerically equal to the mass of water which possesses the same thermal capacity. Hence if W be the water equivalent of the calorimeter and its equipages, as well as of the water w contained, we have

$$W = w + m_1 s_1 + m_2 s_2 + m_3 s_3,$$

where m_1, m_2, m_3 refer to the metal of the vessel, the mercury of the thermometer, and the glass of the stirring-rod and thermometer respectively. When the temperature of the apparatus rises from θ_1 to θ_2, the heat received will be $W(\theta_2 - \theta_1)$, and consequently the equation for the specific heat of the body immersed is

$$ms(\theta - \theta_2) = W(\theta_2 - \theta_1) + R,$$

where R is the correction arising from loss of heat by radiation and conduction during the period of equalisation of temperature.

In general, the terms in W arising from the vessel and its
equipa[illegible]ll compared with the terms representing the water
[illegible] imperfect knowledge of s_1, s_2, s_3 will have little
[illegible]curacy of the results. These quantities may, how-
[illegible]ed by three preliminary experiments, in which the
[illegible] to be glass, mercury, and brass (substance of
[illegible]ly. We [illegible]ll then have three equations, involv-
[illegible]owns, s_1, s_2, s_3, from which they may be determined,
[illegible]wledge of W obtained.
[illegible]oticed that the temperature of the hot body
[illegible]er will always exceed that of the water, and if
[illegible]be a bad conductor of heat, the average Bad conductors.
[illegible] mass may considerably exceed that of the
[illegible]aches its maximum temperature θ_2. For
[illegible]cting substances should be broken into small
[illegible] specific heats are being determined.

[illegible]ion **Correction.**—The equation of the preceding article was de[illegible] on the supposition that a hot body at a temperature θ was placed in a mass of water at a temperature θ_1, and that a common temperature θ_2 was attained. What actually happens, however, is somewhat different. The temperature of the water rises gradually to a *maximum* θ_2. During this process the water loses heat by radiation and conduction, and gains heat from the body immersed. When the maximum temperature θ_2 is first attained the immersed body is still warmer than the water, and heat is being lost

by the water just as fast as it is being received. The temperature remains stationary as long as exact compensation takes place in this manner, and it then begins to fall. Furthermore, the thermometer will always be somewhat behind the water in its indications; during the period of rising temperature its readings will be slightly too low, and when the temperature is falling they will be too high, so that the highest temperature of the water will never be exactly attained by the thermometer. The maximum temperature registered will therefore be slightly below that actually attained by the calorimeter, but the discrepancy will be smaller the quicker the action of the thermometer.

The radiation correction is determined by observing the rate at which the calorimeter cools throughout the range of temperature of the experiment. If the range of temperature be small the radiation may be taken proportional to the difference of temperature between the calorimeter and the surrounding air, and the whole loss by radiation (and conduction) will be approximately equal to that which would occur if the calorimeter had been at its mean temperature $\frac{1}{2}(\theta_1 + \theta_2)$ throughout the whole time of the exper[illegible]t is, the time of rising from θ_1 to θ_2. If the rate of co[illegible] temperature be observed, then, from the known w[illegible] the quantity of heat lost per second at this temperat[illegible] and this multiplied by the time of the experi[illegible] correction R.

Otherwise the interval between the immersio[illegible] and the attainment of the maximum temperatur[illegible] into a series of epochs, t_1, t_2, t_3, etc., at the end of [illegible] temperature of the calorimeter is noted and f[illegible] etc. During the first epoch, t_1, the mean t[illegible] during the second epoch, t_2, the mean ten[illegible] Hence the heat lost during these epochs [illegible] temperature of the air,

$$At_1\left(\frac{\theta_1+\theta'}{2}-\theta_0\right), \quad At_2\left(\frac{\theta'+\theta''}{2}-\theta_0\right),$$

where A is a constant to be determined by observation of the rate of cooling of the calorimeter. This loss of heat by radiation causes a diminution of the maximum temperature θ_2, which can thus be calculated, so that if we write $R = W\Delta\theta$, the maximum temperature which would have been attained by the water would have been $\theta_2 + \Delta\theta$, and the equation for s becomes

$$ms(\theta - \theta_2) = W(\theta_2 + \Delta\theta - \theta_1).$$

The radiation correction increases with the difference of temperature $\theta_2 - \theta_1$, and it is therefore well to arrange that the mass of water placed in the calorimeter shall be so great that the elevation of temperature shall not be very considerable. This, however, diminishes the sensitiveness of the operation, and to counterbalance its effect a very delicate thermometer must be used.

Rumford's method.

The radiation correction may be practically eliminated by a method of procedure suggested by Rumford. Thus, if the highest temperature θ_2 of the calorimeter be approximately known by a preliminary experiment, then if the experiment be commenced by having the initial temperature θ_1 of the calorimeter as much below that of the air of the chamber as θ_2 is above it, heat will be received by the calorimeter during the first part of the experiment, and will be given out during the second; the whole experiment is thus divided into two parts, during one of which its temperature is lower than that of the air, and during the other higher. A complete compensation is not, however, effected by this process. During the first stage the calorimeter receives heat rapidly from the body immersed, and during the second much more slowly. For this reason the first period is much shorter than the second, and the quantity of heat received from the chamber during the first period will be less than that given out during the second.

To secure complete compensation by this method it would be necessary to begin the experiment with the calorimeter at some calculated temperature below that of the chamber, and such that the initial difference of temperature between the chamber and the calorimeter is greater than the final. It may also happen that when the calorimeter is cooled 5° or 6° below the temperature of the air, dew may be deposited on its surface, which will evaporate during the experiment as the temperature rises, and thus lead to a diminution of the final temperature and consequent error in the determination.

Method of stationary temperature.

Another method of avoiding the radiation correction has been recommended by M. N. Hesehus,[1] as practised in the university of St. Petersburg. The principle of the method consists in maintaining the temperature of the calorimeter stationary, and the same as that of the room in which the experiment is made. This is effected by adding cold water gradually to the calorimeter, so as just to counterbalance the heating effect of the body immersed. From the quantity of cold water added the specific heat of the body immersed may be easily calculated. For let θ be the initial temperature of the body im-

[1] Hesehus, *Journal de la Société Physico-chimique Russe*, Nov. 1887; *Journal de Physique*, tom. vii. p. 489, 1888.

mersed, and θ_1 that of the calorimeter. Then, since the calorimeter is kept at θ_1 throughout, it follows that the heat given out by the body immersed is $ms(\theta - \theta_1)$, and if M be the mass of cold water added, and θ_0 its temperature, the heat gained by this water is $M(\theta_1 - \theta_0)$, so that

$$ms(\theta - \theta_1) = M(\theta_1 - \theta_0).$$

It may be observed that in this method the water equivalent of the calorimeter is eliminated as well as the radiation error. The only quantity which it is necessary to observe is the mass M of cold water added to keep the temperature stationary, the temperatures θ, θ_0, θ_1 and the mass m of the body immersed being supposed known.

To effect this in practice an air calorimeter was used. This consisted of a large-bulbed air thermometer, having a brass tube protruding into its bulb somewhat in the manner of the test-tube in Bunsen's ice calorimeter. The hot body was placed in this tube, and cold water was poured in so as to maintain the indication of the manometer constant. In order to avoid errors arising from variations of the temperature of the surrounding air, the air reservoir of the thermometer was placed in a vessel of water at the temperature of the room. Before placing the hot body in the brass tube a weighed quantity of water was placed in it, and the body was then immersed in this water, as in Bunsen's ice calorimeter (p. 217).

130. Regnault's Apparatus.—The apparatus devised by Regnault[1] for the measurement of specific heats by the method of mixtures is shown in Fig. 53. It consists of a heater, C, and a calorimeter, R. The heater is that part of the apparatus in which the substance under experiment is warmed to some known temperature before immersion in the calorimeter. It is simply a form of steam-jacket, comprising three coaxal cylindrical compartments, B, C, D, as shown in section. The body to be heated is placed in a small wire gauze basket, E, and suspended in the inner compartment. This basket possesses two coaxal compartments, the inner of which contains the bulb of a thermometer, and the outer carries the substance to be heated. The inner compartment of the heater in which the basket hangs can be opened at each end. The upper end is closed by a cork through which passes the stem, F, of the thermometer, and also the thread which supports the basket. The lower end, L, of this compartment is closed by a double sliding shutter, which, when open, permits of the basket and the substance which it contains being lowered into the calorimeter by means of the suspending thread G.

The second and third compartments of the heater are traversed by

[1] Regnault, *Ann. de Chimie et de Physique*, 2e, tom. lxxiii. p. 5, 1840.

a current of steam supplied by a boiler, A. The steam enters the second compartment, DD, through H, and after passing through the outer compartment, BB, escapes by the tube M into a condenser. The presence of the steam in the outer jacket prevents cooling and

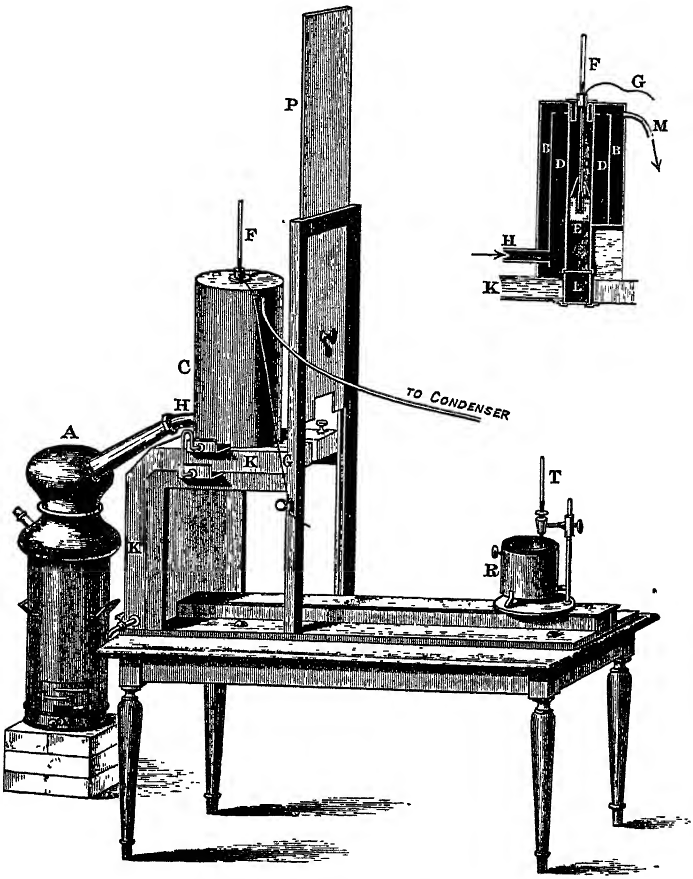


FIG. 53.—Regnault's Apparatus.

condensation in the second compartment, and the temperature of the inner is kept constant, being surrounded by a current of dry vapour.

A considerable time is required before the substance in the basket attains its final temperature. It generally attains a maximum of about 98° C., and should be allowed to remain in the heater for half an hour after its temperature has become stationary. When this has been effected the calorimeter R is run along rails (provided for the purpose) into position under the shutter which closes the lower end of the

inner compartment of the heater. The shutter is then withdrawn, and the basket quickly lowered into the calorimeter. The time occupied in the transference of the basket is so small that no very sensible error can arise through radiation during the passage from the heater to the calorimeter.

In order to prevent radiation to the calorimeter from the heater and boiler during the experiment, the support, KK, on which the heater stands is made hollow, and contains water at the temperature of the air. A thick plate of cork is placed under the heater, so that the water in the supporting stand does not become warm by conduction. A vertical cylindrical aperture is constructed in the stand, so as to permit of the basket being lowered into the calorimeter. While the

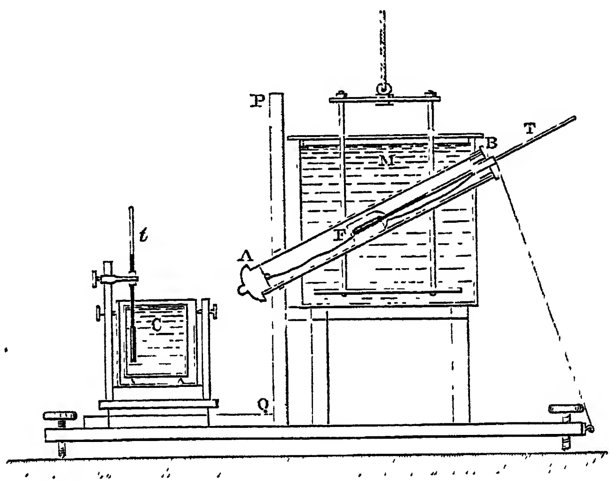


Fig. 54.

substance is being heated the calorimeter is withdrawn to a distance along the rails, as shown in the figure, and a thick cork screen, P, cuts off all radiation from the heating apparatus. This screen is movable, and can be raised when it is desired to run the calorimeter under the heater.

The quantity of water placed in the calorimeter is gauged in a measuring flask of known volume at all temperatures. After the immersion of the heated substance a continual stirring is kept up by agitating the basket by means of the thread employed to suspend it.

With the form of heater described in this apparatus a continuous variation of the initial temperature θ of substance under examination cannot be obtained unless the vapour is produced in a manner which permits of the pressure being varied continuously. Different fixed

temperatures may be obtained by using other liquids than water to furnish the vapour. A continuous variation of the initial temperature may be conveniently obtained by means of a later form of heater employed by Regnault,[1] and shown in Fig. 54. The wire basket containing the substance under examination is placed in a tube AB, running in a sloping direction through an oil bath which can be heated to any desirable temperature. When the temperature of the substance has become stationary it is let down into the calorimeter by means of the thread to which it is attached. The oil bath may be replaced by a freezing mixture, and the specific heat may thus be

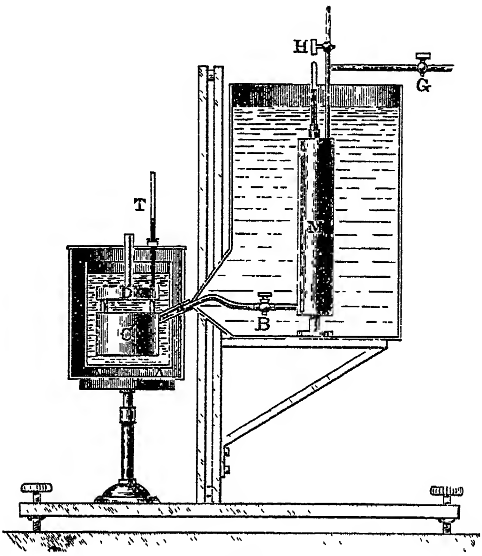


Fig. 55.

determined over a wide range of temperature, and its variations investigated.

131. Specific Heats of Liquids.—The specific heats of liquids and powders and substances soluble in water may be examined by the method of mixtures by sealing them up in thin glass or metal tubes. In the case of bad conductors of heat, however, considerable error may arise from the slowness with which the sealed-up mass yields its heat to the calorimeter, so that not only is the radiation correction enlarged, but it is impossible to determine how far the average temperature of the sealed-up mass differs from the indications of the thermometer both before immersion and at the time of maximum

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. xlvi. p. 270, 1856.

temperature of the calorimeter. In the case of solids, which are poor conductors and soluble in water, another liquid of known specific heat in which they are insoluble may be used in the calorimeter, and the sealing up in a tube can be thus avoided. In the case of liquids, Regnault used the apparatus shown in Fig. 55. The liquid was first heated (or cooled) in a reservoir M, immersed in a bath (or freezing mixture). A tube furnished with a tap, B, led from this reservoir to the calorimeter, where it entered another reservoir, CD, which was completely immersed in the water of the calorimeter. The liquid having attained a definite temperature in the reservoir M, the tap B was opened, and the liquid forced by air pressure, communicated through the tube GH, into the calorimetric reservoir CD. The change of temperature of the calorimeter was noted, and the necessary corrections applied as before. The thermal capacity of the reservoir CD must, of course, be reckoned as part of that of the calorimeter.

132. Favre and Silbermann's Calorimeter.—A special form of calorimeter was devised by MM. Favre and Silbermann,[1] for the purpose of studying thermal phenomena which require some time for completion, such, for example, as the measurement of the quantity of heat evolved during the chemical combination of two or more substances. The principle of the instrument is somewhat the same as that of Bunsen's ice calorimeter, the bulb being, however, filled entirely with mercury, and the heat communicated being measured by the expansion of the mercury in the stem. It is thus a kind of large-bulbed thermometer, the stem of which is bent round at a right angle, so that the part in which the end of the mercury column travels is horizontal, as in the ice calorimeter of Bunsen (Fig. 50). The bulb, which is generally an iron sphere, is fitted with two tubes of glass or platinum, which protrude into the interior of the mercury, and into which the hot body, or the substance under examination, is placed. The bulb is also fitted with a steel plunger, which may be screwed forward into the mercury (or backwards), and by this means the end of the mercurial column can be brought to any part of the stem desired at the beginning of an experiment. The instrument is standardised by introducing a known weight of hot water into one of the tubes and noting the displacement of the index as well as the fall of temperature of the water. If the end of the mercurial column advances n divisions when a mass m of water cools from θ_1 to θ_0, then the heat equivalent of each division of the stem is $m(\theta_1 - \theta_0)/n$. This being known, the heat yielded to the calorimeter during any other

[1] Favre, *Ann. de Chimie et de Physique*, 3^e, tom. xxxvi. p. 5; tom. xxxvii. p. 416; tom. xl. p. 293; 4^e, toms. xxvi., xxvii., xxix.; 5^e, tom. i.

experiment may be inferred from the displacement of the end of the mercurial column in the stem. During an experiment the bulb of the instrument is encased in cotton wool or some other non-conducting stuff, so as to secure uniformity of conditions during all experiments, and to prevent as far as possible loss of heat by radiation and conduction.

The apparatus of Favre and Silbermann has been somewhat modified by M. Jamin,[1] the reservoir of the new instrument being of the form of a glass beaker closed at the top. The stem rises vertically from the top of the reservoir, and the receiving tubes pass down vertically through the top into the interior of the mercury.

A new form of mixing calorimeter specially adapted to the case of liquids has been recently described by Professor S. U. Pickering.[2]

[1] Jamin, *Cours de Physique*, tom. ii., 2e, fasc., p. 17.
[2] S. U. Pickering, *Phil. Mag.*, 5th, vol. xxix. p. 247, 1890.

SECTION IV

THE METHOD OF COOLING

133. Principle of the Method.—The method of cooling in calorimetry is founded on the supposition that when a body cools in a given enclosure the quantity of heat, dQ, emitted by it in a time dt depends only on the excess θ of the temperature of the body above that of the enclosure, and on the nature of the surface of the body. On this supposition we may write down the equation

$$dQ = Af(\theta)dt,$$

where A depends on the surface of the body, that is, on its area and radiating power, and $f(\theta)$ is an unknown function of the difference of temperature, which will be the same for all bodies. Thus, if Newton's law of cooling be true, this function is simply the difference of temperature θ.

Now, if the body cools through an interval of temperature $d\theta$ in the time dt, we have

$$dQ = msd\theta,$$

where m is the mass and s the specific heat of the body, hence

$$msd\theta = Af(\theta)dt,$$

and therefore the time of cooling from a difference of temperature θ_1 to a difference θ_2 will be

$$t = \frac{ms}{A}\int_{\theta_2}^{\theta_1} \frac{d\theta}{f(\theta)} = \frac{ms}{A}\Big[F(\theta_1) - F(\theta_2)\Big].$$

In the same manner, if another body of mass m' and specific heat s' requires a time t' to cool through the same range in the same enclosure, we have

$$t' = \frac{m's'}{A'}[F(\theta_1) - F(\theta_2)],$$

and therefore

$$\frac{t}{t'} = \frac{ms}{m's'} \cdot \frac{A'}{A};$$

and if circumstances can be so arranged that the surfaces of the two

bodies shall be the same, so that $A = A'$, we will have

$$\frac{ms}{m's'} = \frac{t}{t'}.$$

That is, the thermal capacities of the two masses will be in the ratio of the times required to cool through the same range of temperature under the same conditions. We shall now see how far these conditions have been realised in practice.

134. Apparatus of Dulong and Petit.—The first accurate researches by the method of cooling were made by Dulong and Petit. The substance under examination was placed in a small silver vessel and suspended in an enclosure, the walls of which were lamp-blacked and kept at zero by melting ice. The apparatus is shown in Fig. 56. The silver vessel D consisted of two concentric cylinders, the inner of which was just wide enough to contain the bulb of a small delicate thermometer, and the substance was placed in the annular space between the two cylinders. In the case of solids they were finely powdered and tightly packed into this space, so as to be in close contact with its walls. The outside of the silver was brightly polished, so that it might always possess the same radiating power and prolong as much as possible the time of cooling, which is the subject of observation. This time is also extended by exhausting[1] the chamber in which the radiation occurs.

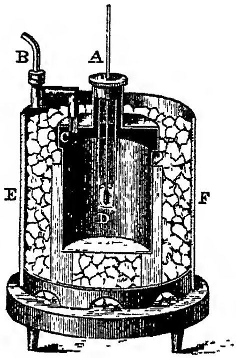


Fig. 56.

In Fig. 56 the silver thimble containing the substance under examination is shown suspended at the centre of an air-tight vessel, the stem of the thermometer, which indicates its temperature, projecting through the top. In making an experiment this vessel is heated, thoroughly desiccated and exhausted, and then surrounded by ice, as shown in figure. The time of falling through some definite range of temperature is then observed—for example, the times of falling from 15° to 10°, and from 10° to 5° C.

The simple equation of the foregoing article becomes somewhat modified when the thermal capacities of the silver vessel and the thermometer are taken into account. Denoting the sum of their thermal capacities by k, the equation becomes

$$\frac{ms+k}{m's'+k} = \frac{t}{t'},$$

[1] The time of cooling was nearly twice as long in vacuum as in air in some of Regnault's experiments.

where k is the same in all experiments, and may be determined by finding t and t' for two substances of known specific heats. It may also be determined by estimating the masses of silver, glass, and mercury respectively, and using their previously-determined specific heats. Both methods were employed by Regnault, but the results were not very concordant. The observation of t and t' for two different masses of water would also lead to a value of k.

135. Regnault's Experiments. — A series of experiments was executed by Regnault[1] with the object of ascertaining how far the method of cooling could be relied on in the estimation of specific heats. In the case of solids the mode of procedure was the same as that of Dulong and Petit, already described. With liquids the experiments were conducted in the same manner, and also with a modified form of apparatus. In the second form of apparatus the silver thimble was dispensed with, and the liquid was enclosed in a small cylindrical bulb of glass, the neck of which was just wide enough to allow a small thermometer to pass down into the liquid within the bulb. The cooling of the liquid was then observed as before.

Method unsuitable for solids.

After an extensive series of experiments on substances whose specific heats had been already determined by the method of mixtures, Regnault was convinced that in the case of solids the method of cooling could not be accepted as a method of sufficient accuracy in calorimetry; and he was forced to this conclusion, not only by the differences between the results obtained by this method and those obtained by other methods for the same substances, but also by the discrepancies existing between the various determinations by this method of the specific heat of the same substance.

With solids the conditions assumed in the deduction of the fundamental equation are never even approximately satisfied. Thus, although the external surface of the silver thimble may always have the same radiating power, yet the contact of the powdered solid with the inside surface will depend on how tightly the powder is pressed into the vessel, and this will not only vary with different substances, but also in different experiments with the same substance. Thus, although we may have $A = A'$ for the external surface of the silver, the communication of heat from the interior outwards will depend both on the conductivity of the powdered solid, and on its contact with the walls of the vessel. For this reason, nothing like equality of temperature can exist throughout the mass, and the temperature registered by the thermometer being that of the interior may be

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. ix. p. 327; and 2e, tom. lxxiii. p. 5.

considerably higher than that of the external silver surface, which is that which should appear in our equations.

In the case of liquids the conditions assumed are much more nearly satisfied. Here the contact with the silver vessel will be much the same in all experiments, and equality of temperature will be fairly established throughout the mass by convection currents, so that the question of conductivity scarcely comes into account. This method is therefore exceedingly convenient in the case of liquids, especially in the case of liquids which cannot be obtained in considerable quantities.

SECTION V

THE METHOD OF CONDENSATION

136. Joly's Steam Calorimeter.—The method of condensation does not appear to have been used in calorimetry, at least with success, until very recently. This probably arose from the mechanical difficulties and the many sources of error which apparently attend this method. In 1886, however, Dr. J. Joly[1] proved that the steam calorimeter was not only an accurate scientific instrument, but that, besides being of more general application, it was probably susceptible of greater accuracy than any other method hitherto employed. He has since proved that in the hands of a skilled experimenter the steam calorimeter gives not only exceedingly consistent and reliable results for solids and liquids, but that by means of it the experimental determination of the specific heats of gases at constant volume, hitherto regarded as impossible, can be readily effected.

The simplest form of Dr. Joly's apparatus consists essentially of a thin metal enclosure, which we shall call the steam-chamber, in which hangs from the arm of a balance a small platinum pan (Fig. 57), carrying the body to be experimented on. Steam is admitted into this chamber at the upper end, through a tube (as shown by the arrows) and escapes through a tube leading from the lower extremity. The steam can be admitted rapidly and shut off at pleasure, or allowed to flow gently through the apparatus.

At the beginning of an experiment a known weight of any substance is placed on the pan, and after remaining some time, so as to take up the temperature of the chamber, its temperature θ_1 is noted by means of a thermometer inserted in a tubulure passing through the side of the steam-chamber. Steam in the meantime is got up in the boiler, and is suddenly admitted, so that the whole chamber becomes at once filled with saturated vapour. Condensation at once begins on the substance, and the resulting water is caught in

[1] J. Joly, *Proc. Roy. Soc.*, vol. xli. p. 352, 1886.

the pan—weights being added to the other pan of the balance so as to restore equilibrium. During this process the steam is admitted very slowly (by opening an escape tube leading from the boiler) into the calorimeter, so that there is no sensible steam draught on the pan, and the weighing is not interfered with. After four or five minutes the substance has attained the temperature of the steam, and the condensation is completed. The pan then ceases to increase sensibly in weight, and the equilibrium of the balance is maintained permanent. A very slow increase of three or four milligrammes per hour (due to radiation) is, however, noticed. Equilibrium having been

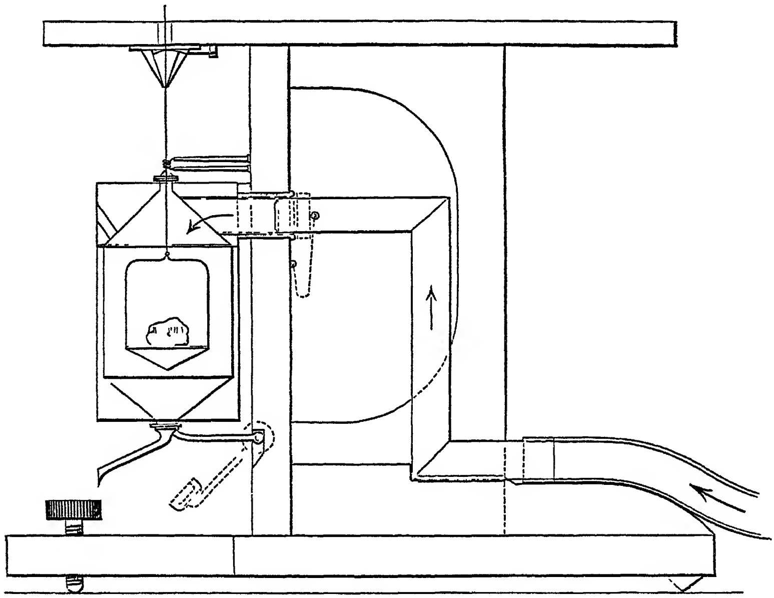


Fig. 57.

obtained, the total increase of weight w is noted, and the experiment is over. Let θ_2 be the temperature of the steam, and L its latent heat. The quantity of heat given out by the condensation is wL, and this is expended in raising the substance and pan from θ_1 to θ_2. If W be the weight of the substance, and s its specific heat, the heat acquired by the substance will be $Ws(\theta_2 - \theta_1)$, and that acquired by the supporting pan will be $k(\theta_2 - \theta_1)$, where k is the thermal capacity of the pan, that is, the quantity of heat necessary to raise its temperature 1° C. Hence we have

$$Ws(\theta_2 - \theta_1) + k(\theta_2 - \theta_1) = wL.$$

The quantity k is determined by a previous observation, and the

temperature θ_2 is found either directly, by a thermometer inserted in the steam chamber, or by means of Regnault's tables and a reading of the barometer.

For extreme accuracy a small correction is still necessary. The weight W of the substance is found in air at θ_1, and the weight w is found when the substance and pan are in steam at θ_2. The weight of steam per cubic centimetre at 100° is little more than half that of air at ordinary temperatures, and for this reason the weight w is greater than the weight of vapour condensed by the excess in weight of a volume v of air at θ_1 over the same volume of steam at θ_2, where v is the volume of the substance and pan together. The difference in weight of a cubic centimetre of air at 15° C. and a c.c. of steam at 100° is ·000636 gramme, according to Regnault; hence, the correction to be applied to w is ·000636v. This correction being applied gives the weight of water condensed, but it must be remembered that it is weighed in steam; and if extreme accuracy be desired, it is still necessary to multiply by the factor 1·000589, in order to reduce the weighing to vacuum. The actual weight in a vacuum of the water condensed will therefore be

$$1{\cdot}000589(w - 0{\cdot}000636v),$$

so that s is determined from the equation

$$(\mathrm{W}s + k)(\theta_2 - \theta_1) = 1{\cdot}000589(w - 0{\cdot}000636v)\mathrm{L}.$$

Where according to Regnault

$$\mathrm{L} = 606{\cdot}5 - 0{\cdot}695\theta_2 - 0{\cdot}00002\theta_2^2 - 0{\cdot}0000003\theta_2^3,$$

or very approximately $\mathrm{L} = 536{\cdot}5 + 0{\cdot}7(100 - \theta_2)$.

In order to avoid the condensation of steam on the suspending wire, where it leaves the steam chamber, it passes, not through a small hole in the metal, but through a small hole pierced in a plug of plaster of Paris. Without the plaster the steam condenses on the metal and forms a drop at the aperture through which the suspending wire passes, and destroys the freedom of motion of the wire and prevents accurate weighing. With the plaster of Paris plug no such drop collects, and the weighing can be performed with accuracy. In his later experiments, Dr. Joly placed a small spiral of platinum wire around the suspending wire just outside the aperture, and by passing an electric current through the spiral, sufficient heat is produced to prevent all condensation on the suspending wire in the neighbourhood of the aperture. Besides accuracy in weighing, a point of prime importance is the rapid introduction of the steam at the beginning of the experiment. When the steam first enters the calorimeter,

partial condensation occurs by radiation to the cold air and the walls of the chamber. Some of the condensed globules may fall upon the substance and lead to an error in the value of s. If the steam enters slowly this error may be large, and it is therefore important to fill the chamber at once with steam. This necessitates a good supply of steam and a large delivery tube, but when the chamber is well filled with steam a very gentle afterflow suffices. If the steam supply be cut off, the weight of condensed vapour slowly diminishes. This arises from distillation over to the colder walls of the chamber, and if the steam be again turned on the weight increases.

The error arising from the deposition of condensed globules on the pan during the initial stages of the experiment is somewhat counterbalanced by radiation from the steam to the substance. This latter is analogous to the transference error in the other methods of calorimetry.

One advantage of the steam calorimeter is that it applies equally to solids, liquids, and gases, and may be used for large or small masses, so as to enable us to find by this means the specific heats of rare substances which are not easily procurable in large quantities. Liquids, powders, and solids acted on by steam may be sealed up in a glass envelope, the thermal capacity of which can be determined. The method therefore appears not only exceedingly accurate, but also universal in its application.

Method of Evaporation.

The method of evaporation, on the other hand, is important in estimating quantities of heat in many scientific investigations. It is particularly useful in evaluating the quantity of heat developed by the combustion of coal or other kinds of fuel, and in measuring the economy of various kinds of furnaces.

137. The Differential Steam Calorimeter — Specific Heats of Gases at Constant Volume.—In a more recent form[1] of the steam calorimeter, the correction for the weight of the steam displaced by the pan is avoided. This form is named the differential steam calorimeter, and has been applied by Dr. Joly to determine the specific heats of gases at constant volume. In this form (shown in front and side view in Fig. 58) two similar pans hang in the steam chamber, one suspended from each arm of the balance, so as to counterpoise each other. The thermal capacities of the pans can be made equal, so that k will vanish from the equation, and the radiation error will also disappear, as it will cause equal condensation on the two pans.

The chief use of the differential form is, however, its application to the calorimetry of gases. For this purpose the pans are re-

[1] J. Joly, *Proc. Roy. Soc.*, vol. xlvii. p. 218, 1889.

placed by two equal spherical shells of copper, one containing the gas at a known pressure and temperature, and the other empty. The spheres are furnished with small pans, or "catch-waters," to collect the water resulting from condensation. Greater condensation occurs on the sphere which contains the gas, and the excess gives the quantity of

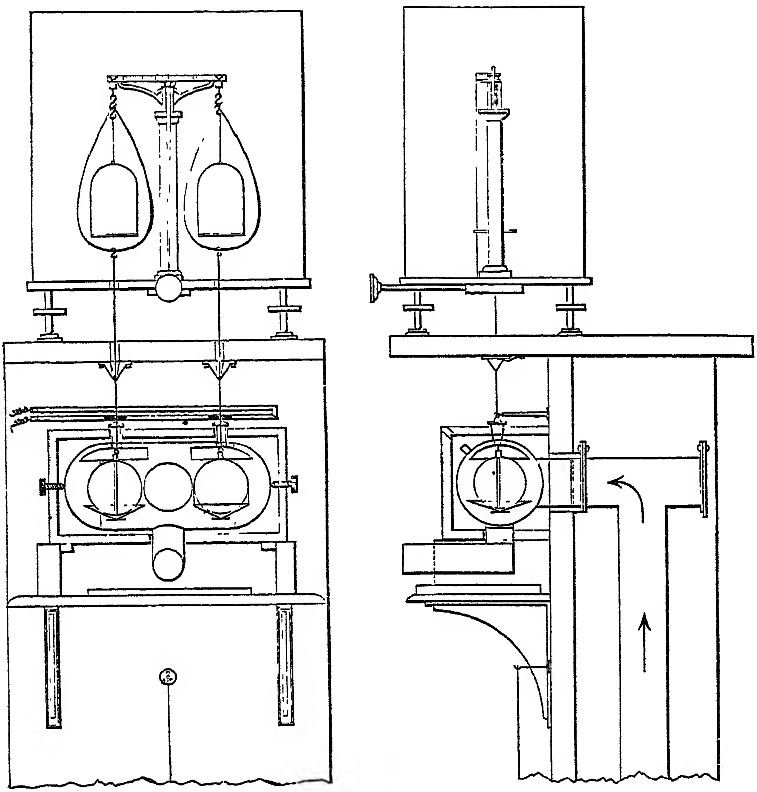


Fig. 58.

heat required to heat the contained mass of gas from θ_1 to θ_2. This determines the specific heat of the gas at constant volume.

The great advantage of the differential calorimeter is, that any source of error common to the two spheres is eliminated, and the gas or other substance enclosed in one of them merely bears its own share of error, and not also that of the containing sphere. Thus an error in the observation of the temperature disappears with regard to the sphere, and the effect is practically the same as if the gas were contained in a vessel of zerothermal capacity in the single steam calorimeter form.

In making an experiment, the sphere used to hold the gas is repeatedly washed out with the dry pure gas, the sphere being both heated and exhausted before each admission of the gas. It is then filled and hung in the steam-chamber and counterpoised against the empty sphere, the difference of weight being noted. This gives the weight of gas enclosed. The stationary temperature θ_1 being noted, the steam is admitted, and in about five minutes the condensation will be complete. The upper temperature θ_2 is then noted. The lower temperature θ_1 is registered by a delicate standardised low-range thermometer, and θ_2 is registered by a similar high-range thermometer. The spheres are now removed from the calorimeter and carefully dried, their high temperature being sufficient to completely evaporate all moisture from their surfaces. When cool, they are again placed in the calorimeter, and equilibrium tested. This is in order to detect if any leakage has occurred during the experiment.[1] Some of the gas may now be let out, and another experiment made with what remains.

The spheres employed by Dr. Joly were of copper, and about 6·7 cm. in diameter, the one containing the gas being made to stand a safe working pressure of about 35 or 40 atmospheres. If at the beginning of the experiment this space is filled with air at about 22 atmospheres at θ_1 the pressure will be about 30 at θ_2. In an experiment the weight of air contained was 4·2854 grammes. The condensation due to the sphere was 1·5 gramme, and that due to the air 0·11629, or about $\frac{1}{13}$ that of the sphere, the range of temperature $\theta_2 - \theta_1$ being 84°·52 C. In a series of six experiments the mean precipitation per degree centigrade was 0·018004.

The corrections necessary for extreme accuracy are—

(1.) Correction for the thermal expansion of the vessel, and the consequent work done by the gas in expanding to this increased volume.

(2.) Correction for the dilatation of the sphere under the increased pressure of the gas as the temperature rises.

(3.) Correction for the thermal effect of stretching of the material of the sphere. Wires are generally cooled by sudden extension, but the cooling of the copper in this case is too small to merit consideration.

(4.) Correction for displacement, or buoyancy, arising from the increased volume of the sphere, both in the air at θ_1 and in the steam at θ_2.

[1] In the later experiments all leakage was completely stopped.

(5.) Correction for unequal thermal capacities of the spheres.
(6.) Reduction of the weight of the precipitation to vacuum.

Dr. Joly's experiments show that in the case of air and carbonic acid the specific heat increases with the density, but with hydrogen the opposite seems to be the case.

For air the specific heat at constant volume at a mean pressure of 19·51 atmospheres, and a mean density of 0·0205 was found to be 0·1721. For carbon dioxide, the change with pressure is shown by the following table :—

Pressure in Atmospheres	Density.	C_v.
7·20	0·011530	0 16841
12·20	0·019950	0·17054
16·87	0·028498	0·17141
20·90	0·036529	0·17305
21·66	0·037802	0·17386

The mean result of the experiments on hydrogen gives a specific heat 2·402.

SECTION VI

ON THE SPECIFIC HEATS OF GASES

138. The Two Specific Heats of a Gas.—It has been already pointed out (Art. 122) that the specific heat of a substance can be spoken of with definiteness only when the conditions under which the heating takes place are stated. If a body be allowed to expand when heated, work will be done against the external pressure, and an equivalent quantity of heat will be required, and if the specific heat be merely defined as the quantity of heat necessary to raise the temperature of unit mass of a substance 1° C., its value will depend on the amount of external work done during the change of temperature, as well as on the nature of the substance. Thus, in general, the specific heat of a substance may have any value whatever if the conditions under which the change of temperature takes place are not defined.

In the case of solids and liquids the change of volume, and therefore the external work done, during change of temperature is small, so that although the specific heats so far determined are those under constant pressure, yet it has not been necessary to allude to the fact. In the case of gases, however, under constant pressure, the change of volume with rise of temperature is considerable, and the thermal equivalent of the external work done during expansion is a large part of the whole heat supplied during the change of temperature. For this reason, the conditions under which the heating of a gas takes place must be stated when referring to the specific heat; and it has become customary to speak of two specific heats in connection with any gas, namely, the specific heat at *constant volume*, and the specific heat under *constant pressure*. The former is the quantity of heat required to raise the temperature of unit mass of the gas 1° C. when its volume is kept constant, and the latter the quantity of heat required to raise the temperature of unit mass 1° C. when the pressure is kept constant. In the former, the pressure increases while the volume is kept constant and no external work is done. In the

latter, the volume increases under constant pressure, and an amount of external work is done which is measured by the product of the pressure by the change of volume.

The experimental determination of the specific heats of gases at constant volume has been already considered under the method of condensation, and we shall now proceed to the experimental determination of the specific heat under constant pressure.[1] This investigation is attended by great difficulties, arising chiefly from the small specific gravities of gases, so that a large volume must be passed through the calorimeter in order to produce any appreciable change of temperature. This requires a considerable time, and during the interval all the causes of error which accompany calorimetric determinations are in operation. The relations connecting the two specific heats, and the methods by which they may be determined indirectly, will be considered afterwards.

139. Specific Heat under Constant Pressure—Regnault's Apparatus.—The apparatus adopted by Regnault to determine the specific heats of gases under constant pressure was a modified form of that used by Delaroche and Bérard. The gas to be operated on was stored dry and pure in a large reservoir, V (Fig. 59), which was immersed in a bath kept at a constant temperature. The pressure of the gas in this reservoir was measured by an open manometer attached to the delivery tube. When the stop-cock R was opened the gas flowed from the reservoir through the spiral tube, immersed in a hot bath EC, which could be maintained at any chosen temperature. This spiral was so long that the gas in passing through it attained the temperature of the surrounding bath. After passing through this spiral the gas entered the calorimeter. Here it passed through a brass reservoir consisting of a series of chambers, and gave up its heat to the calorimeter, emerging finally at the temperature of the calorimeter by the tube D.

The first point of prime importance was to secure a uniform flow of the gas, so that it should pass through the calorimeter uniformly

[1] The first researches on the specific heats of gases were made by Crawford, who applied the method of mixtures and found that the specific heat of air was nearly twice that of water! Afterwards Lavoisier and Laplace (*Œuvres de Lavoisier*, tom. ii.) found by means of their ice calorimeter a more correct value ·33, and subsequently Gay-Lussac (*Ann. de Chimie et de Physique*, tom. lxxxi. p. 98) attacked the subject; but by far the best determinations previous to Regnault's work are those of Delaroche and Bérard (*Ann. de Chimie et de Physique*, 1re série, tom. lxxxv. p. 72), crowned by the Academy of Sciences. They caused a uniform current of gas, heated to 100° C. (by passing through a tube contained in a vapour jacket), to pass through a spiral tube contained in the calorimeter. Joule also made an accurate determination of the specific heat of air (*Phil. Trans.*, pt. i. p. 65, 1852).

and under constant pressure. As the gas escapes the pressure in the reservoir V diminishes, while the pressure outside (the atmosphere) remains constant, consequently the velocity of efflux will gradually diminish. To avoid this Regnault placed a manometer, M, in connection with the conducting tube at N, which registered the pressure at that point. Between this manometer and the reservoir V a screw R was placed (shown enlarged in Fig. 59, *b*B), which obstructed the flow of the gas, but which could be gradually with-

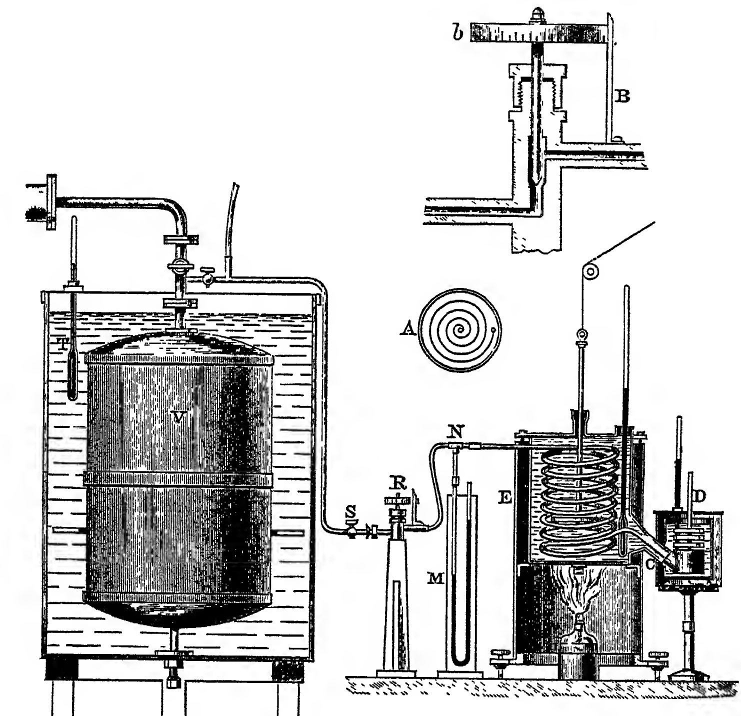


Fig. 59.—Regnault's Apparatus.

drawn so as to leave a wider passage, and keep the pressure registered by M constant. This secured a constant pressure, and hence a uniform flow. Just beyond the manometer the tube was very narrow. In order to make certain that the gas actually acquired the temperature of the bath in passing through the long serpentine EC, Regnault made some preliminary experiments in which a thermometer was placed in the tube, so as to take the temperature of the gas just before leaving the bath. By this means he found that there was no sensible difference of temperature. Hence, in subsequent investiga-

tions the temperature of the gas entering the calorimeter was taken to be that of the bath. Particular precautions were taken to avoid loss of heat by the gas in passing from the bath to the calorimeter, and also to prevent, as far as possible, conduction of heat from the bath to the calorimeter through the connecting tube. For this purpose the connecting parts at C were made of non-conducting material, and the calorimeter was enclosed in a wooden case. It was further necessary to ascertain if the pressure of the gas was the same at entering as at leaving the calorimeter. If that is not the case, the gas will have expanded in the calorimeter, doing work and absorbing heat, and a consequent error will be introduced. Water manometers placed at the entrance C and the exit D showed no more than 1 mm. difference, so that the error arising from this cause was quite insensible. A thermometer placed at D also showed that the temperature of the escaping gas was the same as that of the calorimeter.

It now remained to calculate the weight of gas which passed through the calorimeter during the experiment. In the first place, the total weight of gas in the reservoir is, by Boyle's law, proportional to the pressure if the volume of the reservoir remains constant. This volume was influenced by both temperature and pressure, and to correct the former the reservoir was placed in a bath, and to minimise the latter the reservoir was made strong. For any pressure p Regnault assumed that the weight of gas in the reservoir was given by the formula

$$(1+\alpha\theta)\mathrm{W}=\mathrm{A}p+\mathrm{B}p^2+\mathrm{C}p^3,$$

in which A, B, C were determined by experiment. Thus the weight W′ at any other pressure p' was, at the same temperature,

$$(1+\alpha\theta)\mathrm{W}'=\mathrm{A}p'+\mathrm{B}p'^2+\mathrm{C}p'^3,$$

and consequently their difference w was

$$(1+\alpha\theta)w=\mathrm{A}(p-p')+\mathrm{B}(p^2-p'^2)+\mathrm{C}(p^3-p'^3).$$

By making three such experiments, three values of w, and three equations to determine A, B, C were obtained. These being once determined could be used in all further experiments.

In carrying out an experiment the gas was compressed pure and dry in the reservoir V under a sufficient pressure. The oil bath was heated to a stationary temperature, and a known weight of water was placed in the calorimeter. The whole observation was then divided into three parts.

(I.) The calorimeter was observed for ten minutes in order to determine the heat received per minute through (a) conductivity from

the oil bath; (β) radiation from the screens; (γ) radiation to or from the surrounding air. The effects (α) and (β) are practically constant, for the temperature of the bath is always much higher than that of the calorimeter; but (γ) may be either positive or negative, and must be found by observation of the temperatures of the air and calorimeter from minute to minute. If k represents the change of temperature per minute arising from (α) and (β) together, and if θ_0 be the mean temperature of the air and θ that of the calorimeter during any particular minute, the corresponding change of temperature $\delta\theta$ of the calorimeter arising from the perturbations α, β, γ will be

$$\delta\theta = A(\theta - \theta_0) + k \quad . \quad . \quad . \quad (1).$$

(II.) After the lapse of ten minutes, spent in the observation of the perturbations due to radiation and conduction, the gas was turned on, and during this phase of the experiment the temperature of the calorimeter was changed by the passage of the gas through it, and also, but to a much smaller extent, by the perturbation mentioned in (I.) If the flow is continued for n minutes the total change of temperature arising from the latter causes is

$$\Sigma\delta\theta = A\Sigma(\theta - \theta_0) + nk.$$

If $\Sigma\delta\theta$ be positive it must be subtracted from the final temperature of the calorimeter in order to obtain the temperature which would have been attained if no perturbations existed. Denoting the initial temperature of the calorimeter by θ_1 and its observed final temperature by θ_2, the true final temperature will be $\theta_2 - \Sigma\delta\theta$, and if W denotes the water equivalent of the calorimeter the heat gained by it from the gas will be $W[(\theta_2 - \Sigma\delta\theta) - \theta_1]$, and if w be the weight of gas transmitted, and s its specific heat, the whole mass of gas may be considered as having fallen from the temperature θ of the bath to the mean temperature $\frac{1}{2}(\theta_1 + \theta_2)$ of the calorimeter; consequently the heat lost by the gas will be $ws[\theta - \frac{1}{2}(\theta_1 + \theta_2)]$, and the equation which determines s is

$$ws[\theta - \tfrac{1}{2}(\theta_1 + \theta_2)] = W[(\theta_2 - \Sigma\delta\theta) - \theta_1] \quad . \quad . \quad . \quad (2).$$

(III.) The third part of the experiment consisted in observing the variation of the temperature of the calorimeter for ten minutes after the flow of gas was stopped. It was now only subject to the perturbations, and the change of temperature was due to these causes alone. Denoting the change of temperature per minute of the calorimeter by $\delta\theta'$, and the mean temperature of the air during this minute by θ'_0, while that of the calorimeter is θ', we have

$$\delta\theta' = A(\theta' - \theta'_0) + k \quad . \quad . \quad . \quad (3).$$

This equation, combined with (1), enables us to determine A and k, and hence the quantity $\Sigma\delta\theta$, which, when substituted in (2), gives the specific heat.

In the case of gases which attack copper the spiral tubes were made of platinum, and when pressures higher than the atmosphere were required, the narrowing of the tube just beyond N was dispensed with, and the mouth D of the tube where the gas escaped was made very narrow. The water manometer M was also replaced by a mercurial manometer. The following results were obtained by Regnault:—

SPECIFIC HEATS OF GASES UNDER CONSTANT PRESSURE.
SIMPLE GASES

Air	0·23741	Nitrogen [1] . .	0·24380
Oxygen .	0·21751	Chlorine . .	0·12099
Hydrogen . .	3·4090	Bromine .	0·05552

140. Method of Stationary Temperature.—In the process just described the temperature of the calorimeter varies from θ_1 to θ_2, and may therefore be called the method of variable temperature. Delaroche and Bérard employed in addition the method of stationary temperature. In this method the hot gas is passed through the calorimeter till the temperature of the latter becomes stationary. At this stage the heat gained per second by the calorimeter is equal to that lost by radiation to the surroundings. Denoting the weight of gas which passes through the calorimeter per unit time by w and its specific heat by s, the total heat gained by the calorimeter per unit time will be $ws(\theta-\theta')+k$, where θ' is the stationary temperature of the calorimeter, θ that of the bath, and k the gain of heat by conduction through the connections. But if θ_0 be the temperature of the air, the loss by radiation will be $A(\theta'-\theta_0)$, and consequently

$$ws(\theta-\theta')+k=A(\theta'-\theta_0).$$

The coefficients A and k may be found as before by two observations on the rate of change of temperature of the calorimeter. In determining θ' Delaroche and Bérard warmed the calorimeter initially to a temperature a little inferior to the stationary temperature, and then allowed the gas to pass through, observing the maximum indication of the thermometer placed in the calorimeter, that is, the temperature indicated when it ceased to change by more than $\frac{1}{10}$ of a degree in ten minutes. They then heated the calorimeter a little

[1] The specific heat of nitrogen was deduced from that of air combined with that of oxygen.

above the stationary temperature, and allowed the gas to pass. This time the calorimeter cooled to a stationary temperature. The mean of the two temperatures thus observed they took as the true stationary temperature θ'.

141. Influence of Pressure and Temperature.—It had been supposed by Delaroche and Bérard that the specific heat of a gas depended on the pressure; but Regnault, who investigated this point carefully, found that the specific heat of a gas under constant pressure was sensibly independent of the pressure. This would be expected in the case of a substance rigorously obeying Boyle's law; but in the case of gases like carbonic acid, which deviate considerably from this law, it would not be anticipated. In fact, we have already seen from Dr. Joly's experiments on the specific heat at constant volume that a notable increase of specific heat with density occurs not only in carbonic acid, but also, though to a less degree, in the case of the more perfect gases,[1] while hydrogen behaves in the opposite manner.

The influence of temperature was also studied by Regnault, and for this purpose the bath surrounding the spiral was kept at different constant temperatures, sometimes being replaced by a freezing mixture. He obtained the following results:—

Air.		Carbonic Acid.	
Temperature.	Specific Heat.	Temperature.	Specific Heat
From $-31°$ to $+10°$	0·23771	From $-30°$ to $+10°$	0·18427
$0°$ to $+100°$	0·23741	$+10°$ to $+100°$	0·20246
$0°$ to $+200°$	0·23751	$+10°$ to $+210°$	0·21692

This table shows that the specific heat of air remains sensibly constant, while that of CO_2 rises considerably with the temperature, and it is probable that all gases which deviate from Boyle's law follow the general law of solids and liquids, and show an increase of specific heat with temperature. On the other hand, a perfect gas, when used as a thermometric substance, shows equal rises of temperature for equal increments of heat.

142. Difference of the Two Specific Heats.—A perfect gas is usually considered as an ideal substance whose molecules are outside the sphere of each other's attraction. When such a substance expands no work will be spent in separating the molecules further apart, for by supposition they do not attract each other. The whole work done during a change of volume will consequently be external. Thus, if the volume changes from v_1 to v_2 under a constant pressure p, the

[1] Such an increase, or decrease, becomes quite intelligible when the existence of groups of molecules is recognised as pointed out in Art. 52.

external work is $p(v_2 - v_1)$. Now the specific heat at constant volume C_v is the quantity of heat required to raise the temperature of unit mass 1° C. when the volume is kept constant, and the specific heat under constant pressure C_p will exceed this merely by the thermal equivalent of the work done under constant pressure, while the temperature changes by 1° C. We have therefore

$$J(C_p - C_v) = p(v_2 - v_1) = R(\theta_2 - \theta_1),$$

or, since the difference of temperature is one degree, it follows that

$$J(C_p - C_v) = R.$$

This equation, combined with a knowledge of either specific heat, determines the other, or combined with their ratio, or any other relation connecting them, determines both.

The experimental examination of the assumption made here, namely, that no internal work is done when a gas expands, or rather that in the case of ordinary gases the internal work is very small, was first undertaken by Joule.

143. Joule's Experiment.—In determining the heat developed by compressing air in a vessel, Joule was struck by the accuracy with which it represented the equivalent of the work spent in effecting the compression, and similarly, the quantity of heat lost during expansion appeared to be accurately the equivalent of the work done against the external pressure. He consequently determined to investigate if the temperature of a gas changed when the volume merely increased without doing external work. For this purpose two receivers, A and B (Fig. 60), which were connected together by means of a tube furnished

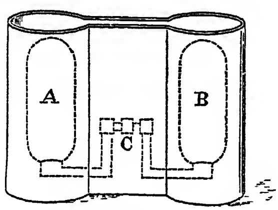


Fig. 60.

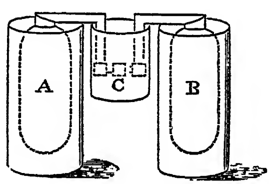


Fig. 61.

with a stopcock, were immersed in a bath of water, which acted the part of a calorimeter. One of the receivers, A, was filled with dry air at about 22 atmospheres, and the other was exhausted. The water was thoroughly stirred, and its temperature noted by means of a very sensitive thermometer reading to $\frac{1}{200}$ of a degree F. The stopcock was then opened by means of a key, and the air allowed to pass from A to B till equilibrium was established. The water was again stirred, and the temperature was found not to have changed by any appreciable

amount. His conclusion was that "no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power."

In order to analyse this experiment, Joule inverted the receivers as shown in Fig. 61, each, as well as the connecting pipe, being immersed in a separate bath. When the air compressed in A was allowed as before to expand into the exhausted vessel B, the temperature of the bath containing A fell, while that containing B rose, as well as that containing the connecting pipe C, the heat lost by A being exactly compensated by that gained by B and C, a small error arising only from those parts of the pipe which were not immersed in water.

From these experiments[1] it follows that no internal work is done by a gas during expansion, or, in other words, the molecules are so far removed from each other as to be practically out of the sphere of each other's attraction. This is not rigorously the case with ordinary gases, which do not accurately obey Boyle's law, but only holds for the ideal perfect gas, to which the permanent gases of nature approximate. The deviations of ordinary gases from the ideal state have been investigated by Joule and Thomson by another method, which will be described later (Chap. VIII.). Joule's law, or Mayer's hypothesis.

144. Fundamental Equation for a Perfect Gas.—We are now in a position to write down the fundamental equations connecting the heat supplied dQ, the change of temperature $d\theta$, and the external work done pdv, during any elementary transformation of a perfect gas. Since there is no internal work, the heat supplied must be all spent in changing the temperature of the gas and in doing external work. The quantity required per unit mass for the former purpose is $C_v d\theta$, where C_v is the specific heat at constant volume. If the volume changes by an amount dv under pressure p, the external work will be pdv, and the thermal equivalent of this is $\frac{pdv}{J}$. Hence the whole heat necessary for the transformation is

$$dQ = C_v d\theta + \frac{pdv}{J}.$$

If dQ and C_v be measured in mechanical units (ergs), or if pdv be expressed in thermal units, the symbol J disappears, and for convenience we shall always suppose that the former system is adopted, and write the equation in the form

$$dQ = C_v d\theta + pdv.$$

[1] An analogous experiment had been previously made by Gay-Lussac (*Mémoires d'Arcueil*, 1807). This method, however, is not susceptible of any extreme delicacy as the thermal capacity of the mass of gas employed must necessarily be small compared with that of the calorimeters.

This equation, combined with the equation $pv = R\Theta$, must furnish the solution of all problems concerning the variations of the properties of a perfect gas under any stated conditions.

145. Adiabatic Transformations.—When the volume and pressure of a substance change while no heat is allowed to escape from it or enter it from outside, the transformations are said to be adiabatic. We are now in a position to determine the relation connecting the volume and pressure of a perfect gas under such conditions. In this case, since heat neither enters nor leaves the substance, we have $dQ = 0$, and therefore

$$C_v d\theta + p dv = 0 \quad . \; . \; . \quad (1).$$

The problem before us now is to find the relation between p and v, that is, to eliminate θ by means of the equation $pv = R\Theta$. From this equation we have

$$p dv + v dp = R d\theta \quad . \; . \; . \quad (2).$$

Substituting for $d\theta$ in (1), and replacing R by its value $C_p - C_v$ (measured in ergs), we obtain

$$C_p p dv + C_v v dp = 0.$$

Or, if γ denotes the ratio of C_p to C_v,

$$\gamma \frac{dv}{v} + \frac{dp}{p} = 0,$$

which, by integration, gives at once

$$\gamma \log v + \log p = \text{const.}$$

That is

$$pv^\gamma = \text{const.} \quad . \; . \; . \quad (3),$$

which is the required relation between p and v.

Combining equation (3) with the characteristic equation of the gas $pv = R\Theta$, we obtain the adiabatic relations between the pressure and temperature, and between the volume and temperature. Thus

$$\Theta p^{\frac{1-\gamma}{\gamma}} = \text{const.} \quad . \; . \; . \quad (4),$$

and

$$\Theta v^{\gamma - 1} = \text{const.} \quad . \; . \; . \quad (5).$$

146. Ratio of the Two Specific Heats of a Gas.—Until the perfection of steam calorimetry by Dr. Joly, no successful measurement of the specific heat of a gas at constant volume was effected. The specific heat under constant pressure was determined by the methods already described, and from this the specific heat at constant volume was evaluated by means of further considerations of the properties of gases; such, for example, as the formula of Art. 142 for the difference of the specific heats. Another method follows from the theoretic formula

for the velocity of sound in air. Laplace showed that the velocity of sound in a gas is determined by the formula

$$v=\sqrt{\gamma\frac{\mathrm{P}}{\mathrm{D}}},$$

where P is the pressure, D the density, and γ the ratio of the two specific heats. Hence a knowledge of v, P, and D gives a determination of γ, which leads at once to the value of C_v when C_p is known. By this method the value $\gamma = 1{\cdot}408$ has been found for air.

147. Method of Clément and Desormes.—The adiabatic equation, $pv^\gamma = \text{const.}$ leads to an experimental determination of γ first devised

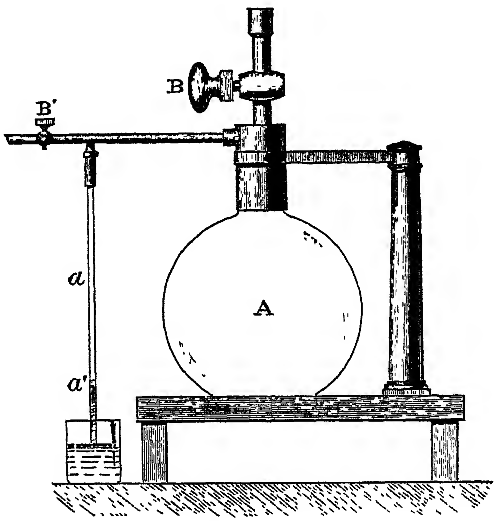


Fig. 62.

by MM. Clément and Desormes.[1] A large flask (Fig. 62) is furnished with a very wide stopcock B, which communicates with the exterior air, and also with a sensitive water[2] manometer aa'. Initially the flask A is partially exhausted, so that the liquid stands at a level a in the manometric tube. The cock B is then suddenly opened for a short interval, and again closed. During this interval the air rushes into[3]

[1] *Journal de Phys. de Delamétherie*, tom. lxxxix. p. 333, 1819. See also Laplace, *Mécanique Céleste*, tom. v. p. 148, etc. From the measurements of Clément and Desormes, Laplace deduced the value $\gamma = 1{\cdot}354$.

[2] Sulphuric acid would be less objectionable.

[3] The converse method in which the pressure within the flask was initially greater than that of the atmosphere, so that an outrush occurred when the tap was opened, was first used by Gay-Lussac and Welter. See Ostwald's *Outlines of General Chemistry*, p. 75.

the flask, and the pressure within becomes equal to that outside; the temperature, however, is elevated inside in consequence of the inrush of air. The tap B being closed, the air in the flask cools, and, as a consequence, the internal pressure diminishes, and the liquid, which, at the closing of the tap B stood at the bottom of the tube, now rises to a height a'.

Let the pressure of the atmosphere be p_0, that of the air in the flask p_1 before opening B, and p_2 finally after the air has cooled to its original temperature.

Then, since the first process occurs so rapidly that it may be regarded as adiabatic, we have for a unit mass of air in the flask before and after opening B

$$p_1 v_1^\gamma = p_0 v_0^\gamma.$$

Hence,

$$\gamma(\log v_1 - \log v_0) = \log p_0 - \log p_1.$$

But since the initial and final temperature are the same,

$$p_1 v_1 = p_2 v_0;$$

since the manometer tube is narrow, the volume of the unit mass of the gas will not be appreciably altered by the small rise of the liquid in the tube. Hence $v_1/v_0 = p_2/p_1$, and

$$\gamma = \frac{\log p_0 - \log p_1}{\log p_2 - \log p_1},$$

the quantities p_0, p_1, p_2 being noted, the value of γ is obtained.

This method is open to serious objections, for it is difficult to arrange the experiment so that the pressure within the flask shall be exactly equal to the external pressure at the instant the cock is closed, while at the same time the operation must be conducted so quickly that no sensible quantity of heat has been communicated by the air within to the sides of the flask. When the stopcock is opened there is an over-rush[1] of air, and an oscillation is set up, that is, more air rushes in at first than would fill the flask at the external pressure. A back-rush then sets in and an oscillation to and fro of air takes place through the orifice. Consequently, when the tap is closed the pressure within the flask may be either greater or less than the external pressure, unless sufficient time has been allowed for the oscillatory motion to subside. When the stopcock B is wide this inconvenience is to a great extent avoided. By this means M. Röntgen[2] found the value $\gamma = 1{\cdot}4053$.

In order to secure good results, dry air should be used as well as

[1] Cazin, *Ann. de Chimie*, 3e, tom. lxvi. p. 206.

[2] Rontgen, *Pogg. Ann.* vol. cxlviii. p. 580, 1873.

M. Leray[1] has recently endeavoured to show that the product of the molecular weight w and the *absolute* specific heat C_a (see Art. 123) is the quantity which has the same value for all substances. In the case of a few gases, he has calculated the absolute specific heat from an approximate formula, and the product wC_a, as shown in the following table. In the case of solids and liquids the absolute specific heat cannot be found, and for these the law cannot be verified.

Gas.	w.	C_a	wC_a
H_2	2	0 743475	1·486950
N_2	28	0 053156	1·488368
CO_2	44	0 034131	1·501764

150. Extensions of Dulong and Petit's Law—Molecular Thermal Capacities.—An extension of the law of Dulong and Petit, by which the specific heat of a compound might be inferred from those of its constituents, was suggested by Woestyn,[2] on the supposition that the atoms, when in combination, preserve their original thermal capacities, and consequently that the thermal capacity of a molecule of any compound is equal to the sum of the thermal capacities of its constituents. Thus, if there be n_1, n_2, n_3, etc., atoms of atomic weights w_1, w_2, w_3, etc., in the molecule, then the molecular weight is

$$W = n_1w_1 + n_2w_2 + n_3w_3 + \text{etc.},$$

and if the specific heats of the constituents be s_1, s_2, s_3, etc., while that of the compound is s, we have under the supposed condition

$$Ws = n_1w_1s_1 + n_2w_2s_2 + n_3w_3s_3 + \text{etc.} \quad . \quad . \quad . \quad . \quad (1)$$

In this equation w_1s_1, w_2s_2, etc., are the thermal capacities of the corresponding atoms, and if these are each equal to the mean value 6·38 given by Dulong and Petit's law, we have

$$Ws = (n_1 + n_2 + n_3 \ . \ . \ . \ )6{\cdot}38 = 6{\cdot}38N,$$

a formula which has been verified by Regnault[3] in the case of metallic alloys, the constituents of which were taken in proportions which were multiples of their atomic weights. The constant 6·38

[1] Leray, *Ann. de Chimie et de Phys.*, 6e, tom. xxv. p. 89, 1892.
[2] Woestyn, *Ann. de Chimie et de Phys.*, 3e, tom. xxiii. p. 295, 1848.
[3] Regnault, *Ann. de Chimie et de Phys.*, 3e, tom. i. p. 129, 1841.

was, however, not maintained, but increased considerably when the temperature approached the fusing point of the alloy.

The general equation (1), being supposed established, may be employed to determine the specific heat of any element in combination with others of known specific heats. Thus, if all the quantities which occur in the equation be known except s, then the value of s becomes determined. By this means H. Kopp[1] has shown that, as previously announced by Garnier,[2] the specific heat of water in combination in the various hydrates is the same as that of ice, that is, water substance in the solid state.

Neumann's law.

While investigating the specific heats of compounds of the same general formula Neumann[3] found that the product of the molecular weight and specific heat remained constant for all compounds belonging to the same general formula and similarly constituted, but that the product varied from one series to another. This is known as Neumann's law.

151. Variation of Specific Heats with Temperature.—The considerations brought forward in Art. 52 lead us to suspect that the specific heat of any substance may change (either increase or decrease) as the temperature varies. The idea that the specific heat of a substance is not the same at all temperatures seems to have been suggested by Dalton. He supposed that a certain quantity of heat was employed in producing the dilatation which accompanies changes of temperature in bodies, and that therefore as the dilatation for 1° change of temperature varies, the quantity of heat necessary to effect the change of temperature must vary also. He concluded, consequently, that the thermal capacity of a given mass of a substance varied with the temperature, but that the thermal capacity of a definite volume remained constant. This idea, however, was not founded on any experimental investigation of the variations of specific heat with temperature, and it can therefore only be regarded as a conjecture. The first comprehensive series of experiments on the subject were made by Dulong and Petit,[4] who found that the specific heats of all the substances examined by them increased gradually with the temperature, and the general truth of their conclusions has been confirmed by the results of the experiments made by all subsequent investigators.

The law which governs the variations of specific heat with tempera-

[1] Liebig, *Ann.*, Supplement, vol. iii. pp. 1 and 289.

[2] Garnier, *Comptes Rendus*, tom. xxxv. p. 278, 1852.

[3] F. E. Neumann, *Pogg. Ann.*, vol. xxiii. p. 1, 1831.

[4] Dulong and Petit, *Ann. de Chimie et de Physique*, 2e, tom. vii. p. 147; tom. x. p. 395.

ture is, however, still unknown. It has been merely ascertained that the specific heat in the vast majority of cases increases with the temperature, and may be represented by some general formula of the type

$$s=a+b\theta+c\theta^2+\text{etc.},$$

where the coefficients, a, b, c, etc., must be determined for each series of experiments, and the formula then cannot be regarded as containing any law which applies beyond the range of the series, but must be regarded merely as a convenient mode of representing the results of a particular series of experiments with more or less approximation.

The majority of solids exhibit only a small increase of specific heat as the temperature rises, until the melting point is approached. Near the melting point, however, the specific heat may change rapidly, especially in the case of amorphous substances which pass gradually into the liquid state, as already noticed in Art. 122. A few substances, however, show large variations of specific heat with temperature, and the most noted of these is carbon, which exists in several varieties. Numerous experiments have been conducted from time to time on the specific heats of the several varieties of carbon, chiefly on account of the wide deviation of this element from the law of Dulong and Petit. The results obtained by different observers are given in the following table, and the discrepancies between the several values obtained for the same substance appeared to F. Weber[1] to be quite too large to be accounted for by experimental errors or impurities, and that they must depend upon some source of variation of specific heat, such as change of temperature.

Observer.	Wood Charcoal.	Gas Coal	Native Graphite.	Furnace Graphite.	Diamond.	Temperature Interval.
Regnault .	0·2415	0·2036	0·2017	0·1970	0·1469	8° to 98°
De la Rive and Marcet	0·2009	...	. .	. .	0·1146	3° to 14°
Kopp . .	...	0·185	0·174	0·165	...	22° to 52°
Wüllner and Bettendorf	...	0·2006	0·1919	0·1920	0·1452	22° to 70°

It may be noticed from the table that the specific heat is less for

[1] F. Weber, *Pogg. Ann.*, vol. cliv. pp. 367, 553; *Phil. Mag.*, vol. xliv. p. 251, 1872.

the crystalline variety diamond than for the porous varieties,[1] and that assuming the correctness of the experimental work, those determinations which were conducted at the lower temperatures gave the lesser specific heat, and this suggests a rapid increase of specific heat with the temperature.

To test this point Weber executed a careful series of experiments at different temperatures with Bunsen's ice calorimeter, and found that the mean specific heat of diamond between 0° and θ° may be represented by the formula

$$s_m = 0{\cdot}0947 + 0{\cdot}000497\theta - 0{\cdot}00000012\theta^2$$

between 0° and 200° C.

The specific heat s at any temperature θ will therefore be found from the equation

$$s_m = \frac{1}{\theta}\int_0^\theta s\,d\theta.$$

That is

$$s = 0{\cdot}0947 + 0{\cdot}000994\theta - 0{\cdot}00000036\theta^2.$$

Thus, at 200° C. the specific heat of diamond is more than three times its value at zero.

For temperatures above 200° C. the water calorimeter was used, but the experiments were not so reliable. Similar variations were found in the case of silicon and boron, so that, although these elements seemed at first to overthrow the generality of Dulong and Petit's law, the large variations of specific heat with temperature show us that the applicability of the law to any element depends on the temperature at which the specific heat is determined.

Among liquids, alcohol appears to change considerably in specific heat, and according to the experiments of Hirn attains a value 1·11389 at 160° C., which is superior to that of water at 100° C. The whole question of variation of specific heats with temperature still calls for further investigation.

The following table contains the results of Regnault's experiments on a few liquids :—

[1] This, as Dr. Joly has observed, appears to hold for several other crystalline substances (*Proc. Roy. Soc.*, vol. xli. p. 250, 1886).

Liquid.	Quantity of Heat $Q=\int s d\theta$.	Range of Temperature.
Water . . .	$\theta+0\cdot00002\theta^2 + 0\cdot0000003\theta^3$	0° to 200°
Alcohol . . .	$0\cdot54755\theta+0\cdot0011218\theta^2 + 0\cdot000002206\theta^3$	– 23° to + 66°
Essence of turpentine	$0\cdot41508\theta+0\cdot00061935\theta^2 - 0\cdot0000013274\theta^3$	0° to 150°
Carbon bisulphide .	$0\cdot23523\theta+0\cdot000081516\theta^2$	– 30° to + 40°
Ether . . .	$0\cdot52899\theta+0\cdot00029587\theta^2$	– 20° to + 30°
Chloroform . .	$0\cdot23234\theta+0\cdot000050711\theta^2$	– 30° to + 60°

152. Influence of Change of Density and State.—Besides the large changes of specific heat which occur when a body passes from the solid into the liquid or gaseous conditions, it is found that other small variations accompany such alterations as the changes of density of solids caused by hammering. As a general rule, the specific heat of a metal is diminished when the density is increased by hammering, but in many cases the changes are negligible. Thus in the case of steel, lead, and tin, hammering does not sensibly affect the specific heat, but in the case of annealed copper the specific heat is reduced from 0·09501 to 0·0936 by hammering.

A more marked difference occurs in the specific heats of the allotropic varieties of some substances. Thus, for carbonate of calcium in the state of aragonite or spar it is 0·2085, and for chalk it is 0·2148, and for marble 0·2158. The case of carbon in its different varieties has been mentioned in the previous article, and on account of the variations of specific heat with temperature, it is very probable that there are temperatures at which the specific heats of the allotropic varieties of all substances are the same. In the case of carbon Kopp surmised that the difference between the specific heats of the opaque varieties and diamond arose from the action of gases and vapours condensed in the pores of these varieties, and to the heating action which occurs when porous substances are immersed in water. In order to test this point Wüllner and Bettendorf conducted a series of experiments in which the heating action arising from the moistening of the porous varieties was avoided. They found, as shown in the foregoing table, that the specific heats of the opaque varieties are not equal to that of diamond, and that Kopp's assumption was not justified. According to Weber, however, all the opaque varieties of carbon have the same specific heat when proper precautions are taken to avoid moistening the porous varieties by enclosing them in sealed glass tubes during the experiment. At the temperature of

red-heat, when diamond is not distinguishable from the other varieties, Weber considered that the specific heats of all are equal, and that this rule applies to all other polymorphous bodies.

The specific heat of a substance is generally very different in the three states of matter—solid, liquid, and gaseous. In general, the specific heat in the solid state is much less than in the liquid, but sometimes the specific heat of the gas is very nearly the same as that of the solid. For example, the specific heat of water is nearly twice that of ice or of water vapour. This is shown by the following table:—

	Solid.	Liquid.	Gas.
Bromine	0·08432	0·107	0·05552
Water	0·474 0·504	1·000	0·477
Mercury	0·03136	0·3332	...
Phosphorus	0·1740 0·1887	0·2405	
Tin	0·05623	0·0637	
Bismuth	0·0308	0·0363	.
Lead	0·0314	0·0402	..
Iodine	0·0541	0·1082	.
Alcohol	.	0·5475	0·4534
Bisulphide of carbon		0·2352	0·1569
Ether		0·5290	0·4797

For the metals the change of specific heat arising from fusion is small, being of the same order as the change of specific gravity.

153. Specific Heat of Water.—One of the most important researches in the whole range of calorimetry is the accurate investigation of the variations of the specific heat of water, especially between 0° and 100° C. If the unit of heat be defined as the quantity necessary to raise the temperature of unit mass of water from 4° to 5° C., then if the thermal capacity of unit mass be not the same at all temperatures, and if the variations with temperature be not known, it would be necessary in any experiment to always start with as much water in the calorimeter at 4° C. as would just attain the final temperature of 5° C. The quantity of water employed (together with the equivalent of the calorimeter, etc.) would then represent the quantity of heat given out by the immersed body in cooling from its initial temperature to 5° C.

The direct mode of investigating the variations of the specific heat of water is that adopted by the earliest experimenters on this subject (De Luc and Flaugergues), namely, by mixing known weights of water

at different temperatures and observing the temperature of the mixture. By this method Flaugergues[1] found that the specific heat of cold water was slightly greater than that of warm water, as shown by the following numbers, temperature being in degrees Réaumur :—

3 parts of water at $0° + 1$ part at $80°$ gave $19°{\cdot}86$ R.
2 parts of water at $0° + 2$ parts at $80°$ gave $39°{\cdot}81$ R.
1 part of water at $0° + 3$ parts at $80°$ gave $59°{\cdot}87$ R.

It does not appear certain, however, that due precautions were taken to guard against errors arising from radiation and evaporation, or to correct for the thermal capacity of the calorimeter.

The first experiments of any accuracy were those of F. E. Neumann,[2] who found in 1831 that the specific heat of water at the boiling point was about 1·0127 times that at 28° C. The next experiments were those of Regnault[3] in 1840, from which he deduced that the mean specific heat between 15° C. and 100° C., compared with that between 10° and 15°, was from 1·00709 to 1·0089. He further extended his researches to temperatures above the boiling point, and found that the results of his experiments at temperatures up to 230° C. were represented by the formula

$$s = 1 + 0{\cdot}00004\theta + 0{\cdot}0000009\theta^2.$$

This formula indicates a gradual increase of specific heat as the temperature rises.

Somewhat later Pfaundler and Platter[4] supposed that they had discovered important variations in the specific heat of water in the neighbourhood of the temperature of maximum density. They estimated that it fell from unity at zero to 0·9512754 at 1°, and then increased gradually to 1·1933497 at 6°·5, and afterwards fell to 1·0728772 at 10° C. The method of mixtures was employed, but almost immediately afterwards it was shown by the investigations of Hirn, as well as those of MM. Jamin and Amaury, that no such variations occur. The method adopted by Hirn[5] was excellent and ingenious in design, but difficult to carry into execution with accuracy. It consisted essentially in supplying equal quantities of heat to a given mass of water when at different temperatures, and observing

[1] Quoted by Rowland, *Proc. American Academy of Arts and Sciences*, vol. vii. p. 120, 1879-80.

[2] Neumann, *Pogg. Ann.*, vol. xxiii. p. 40, 1831.

[3] Regnault, *Relation des Expériences*, tom. i. p. 729 ; or *Mémoires de l'Académie des Sciences*, tom. xxi.

[4] Pfaundler and Platter, *Pogg. Ann.*, vol. cxl. p. 575 ; vol. cxli. p. 537, 1870.

[5] Hirn, *Comptes Rendus*, tom. lxx. pp. 592, 831, 1870.

the change of temperature. The method by which the equal quantities of heat were supplied was by heating a large water thermometer, with a metal bulb of about 200 c.c. capacity, and then immersing it in the calorimeter till the column in its stem fell through a certain interval, when it was at once withdrawn. The change of temperature of the calorimeter by this communication of heat was only about 1° or 1°·5 C., and the chief difficulty was to estimate this change with accuracy. In the method[1] adopted by Jamin and Amaury[2] the water was heated by the passage of an electric current through a spiral of wire immersed in it, and if proper precautions were taken in the observations, and due allowance made for the variation of the resistance of the spiral with temperature, the method should be capable of giving excellent results. The formula deduced as representing the results of their experiment was

$$s = 1 + 0{\cdot}0011\theta + 0{\cdot}0000012\theta^2.$$

This formula indicates a gradual increase of specific heat as the temperature rises, but the amount of variation indicated is exceedingly high.

The first experiments of sufficient accuracy to discover the true nature of the variations of the specific heat of water were those made by Rowland in his exhaustive determination of the dynamical equivalent of heat. If it be assumed that the value of the dynamical equivalent, determined by means of the friction of a liquid of assumed constant specific heat, must be the same whatever the initial temperature of the liquid, then if variations in its value are observed when the liquid is used at different temperatures, these variations must be attributed to changes of the specific heat of the liquid. In operating through a wide range of temperature Rowland found that the values of J obtained at different temperatures indicated that the specific heat of water fell to a minimum at about 30° C. That is, that the specific heat of water did not gradually increase from zero, but that a gradual diminution occurred up to about 30° C., and then a gradual increase set in. This point was further tested and placed beyond doubt by actual calorimetric observations of the most careful nature, the apparatus employed for this purpose being similar to that designed by Regnault (Fig. 55) for the determination of the specific heats of

Minimum for water.

[1] The method of generating equal quantities of heat in two calorimeters by means of an electric current, and thus comparing the specific heats of two liquids, was first suggested by Joule as an accurate method in calorimetry.—Joule, *Mem. Manchester Phil. Soc.*, vol. vii. p. 559, 1845.

[2] Jamin and Amaury, *Comptes Rendus*, tom. lxx. p. 661, 1870.

liquids. The results obtained by the dynamical equivalent apparatus are, in Rowland's opinion, of surpassing accuracy (see Chap. VIII. Sec. i.).

The work of Rowland has been quite recently confirmed by Bartoli and Stracciati,[1] who find a minimum value of the specific heat at 20° C., the specific heat being taken unity at 15° C. The results of their experiments are contained in the following table, in which s_θ represents the specific heat at $\theta°$, and $s_{0\theta}$ the mean specific heat between 0° and $\theta°$.

θ.	s_θ	$s_{0\theta}$.	θ.	s_θ.	$s_{0\theta}$
0°	1·00664	1·00664	16°	0·99983	1·00264
1°	1 00601	1·00632	17°	0·99968	1·00247
2°	1·00543	1·00607	18°	0·99959	1·00231
3°	1·00489	1·00573	19°	0·99951	1·00216
4°	1·00435	1·00545	20°	0·99947	1 00203
5°	1·00383	1·00518	21°	0·99950	1·00191
6°	1·00331	1·00491	22°	0·99955	1·00180
7°	1·00283	1·00465	23°	0·99964	1·00171
8°	1·00233	1·00439	24°	0·99983	1·00162
9°	1·00109	1·00414	25°	1·00005	1·00155
10°	1 00149	1·00389	26°	1·00031	1·00150
11°	1·00111	1·00366	27°	1·00064	1·00146
12°	1·00078	1·00343	28°	1·00093	1·00144
13°	1·00048	1·00321	29°	1·00143	1·00143
14°	1·00023	1·00301	30°	1·00187	1·00144
15°	..	1·00283	31°	1·00241	1·00147

The specific heat of a saturated vapour is discussed in Chap. VIII. Sec. vi., and the case of a non-saturated or superheated vapour is noticed in Art. 176.

[1] A. Bartoli and E. Stracciati, *Boll. mens. dell' Acc. Gioenia,* 18, 26th April 1891. *Beiblätter zu den Annalen der Physik und Chemie,* Band xv. p. 761, 1891.

CHAPTER V

CHANGE OF STATE

SECTION I

FUSION

154. Normal Fusing Point.—When the temperature of a solid is gradually raised, a stage is reached at which the substance passes into the liquid state. For each crystalline substance there is, generally speaking, a definite temperature at which, under given conditions, it passes from the solid to the liquid state, or *vice versâ*. That is, when the temperature is above this point the substance exists in the liquid state, and below it in the solid state. This temperature is called the fusing point (or the melting point) of the substance under the given conditions, and is such that when the temperature of the solid is rising liquefaction occurs here, and when the temperature of the liquid is falling solidification sets in at the same point. Thus at 0° C. ice melts and water solidifies under the pressure of one atmosphere, and 0° C. is said to be the normal fusing point of ice. We say the *normal* fusing point, for circumstances may occur, as we shall see later on, under which water may not solidify even though its temperature is considerably below 0° C. Similar abnormal results are presented by other substances, the liquid state often persisting at a temperature considerably below that at which the substance ordinarily solidifies.

In the case of ice the melting point is distinct and sharply marked. There is no perceptible difference of temperature between the melting solid and the liquid into which it passes. At 0° C. water substance can exist in three very distinct forms, either as a hard solid, a mobile liquid, or an attenuated vapour. It is very different, however, with many other substances. In the case of fats, wax, glass, iron, and other amorphous substances, there is no definite point, sharply marked, at Amorphous solids. which it can be said the substance melts. As the temperature of the solid rises the substance becomes more and more plastic. It gradually attains a semi-solid viscous condition, in which it possesses neither the properties of a solid nor of a liquid distinctly. The process of fusion is

gradual, and the body passes by no sudden transition from the solid to the liquid state.

Crystals. This gradual passage from the solid to the liquid state is characteristic of amorphous bodies, whereas those which crystallise on solidification have in general a definite fusing point at which the substance may exist simultaneously in the two states. It is only solids having a crystalline structure that have a definite melting point, and at other temperatures only one of the states is stable. At this temperature the molecules arrange themselves in the regular order which determines the crystalline structure.

In amorphous bodies, on the other hand, there is no definite arrangement of the molecules at any temperature, the amorphous condition of the solid forms a continuation of the liquid state as far as want of regular molecular arrangement is concerned, and such substances have no definite melting point.

155. Laws of Fusion.—The general laws which govern the phenomena of fusion and solidification may be summarised as follows :—

(1) For a given pressure the temperature of fusion is fixed, and is the same as that of solidification, and consequently, while fusion (or solidification) is taking place the temperature of the whole mass remains constant.

(2) During fusion heat is absorbed by the substance (latent heat), and an equal quantity of heat is disengaged during solidification.

156. Surfusion—Unstable Condition.—A liquid which has a definite freezing point—that is, one which crystallises on solidifying, may, if carefully and slowly cooled, be reduced to a temperature much below the normal freezing point without solidification setting in. This anomalous condition is, however, unstable, for if the over-cooled liquid be disturbed, or if a small piece of the crystalline solid be placed in contact with it, solidification at once sets in and continues until the temperature rises to the normal freezing point.

This phenomenon of surfusion, as it is termed, was noticed as early as 1724 by Fahrenheit.[1] He found that a glass bulb filled with water and hermetically sealed remained at a temperature considerably below the freezing point without solidification setting in, but that on breaking off the stem solidification set in with rapidity. Gay-Lussac[2] also observed that water placed in a vessel and covered with a layer of oil remained liquid at $-12°$ C., but a slight shake was sufficient to start solidification. Despretz[3] observed the same effect in capillary tubes

[1] Fahrenheit, *Phil. Trans.*, vol. xxxviii. p. 78, 1724.

[2] Gay-Lussac, *Ann. de Chimie*, 2^e, tom. lxiii. p. 363, 1836.

[3] Despretz, *Comptes Rendus*, tom. v. p. 19, 1837.

filled with water; and it is perhaps for this reason that at low temperatures the sap often remains unfrozen in the capillary vessels of plants.

This property is not peculiar to water. It may be observed in many other substances when the cooling is conducted cautiously. In the case of melted phosphorus cautiously cooled below the freezing point, a fragment of amorphous phosphorus is found to be inactive in producing solidification, while a fragment of ordinary phosphorus at once starts congelation. The introduction of a fragment of the solid is not in general necessary to set up solidification in the over-cooled liquid. Mechanical actions, such as the vibration caused by the friction of a glass rod against the bottom of the containing vessel, suffices in general to initiate solidification.

As soon as solidification sets in there is an evolution of heat, and the freezing continues till the heat evolved is sufficient to bring the whole mass to the normal fusing point. Further solidification will now cease, unless the substance continues to lose heat by radiation or otherwise.

This property has been utilised by M. Gernez[1] and others to determine the normal temperature of fusion. The liquid under examination is cautiously cooled to a temperature below the normal fusing point. Solidification is then excited, and part of the substance separates in the solid form, the temperature at the same time rising to that of normal fusion. This is noticed by means of a thermometer placed in the substance.

M. Dufour[2] contrived to cool small spherules of water to $-20°$ C. without solidification. The method adopted was similar to that employed by M. Plateau in the study of the equilibrium of liquids relieved from the action of gravity. Small droplets of the liquid were suspended in another liquid of equal density and lower freezing point. The suspended drops were thus freed from the action of gravity, and floated freely in the bath as spherical globules. In this manner M. Dufour succeeded in reducing to $-20°$ C. the temperature of water droplets suspended in a mixture of chloroform and oil of sweet almonds. The temperature of similar drops was also raised as high as 178° C. without boiling, while drops of liquid sulphur were reduced below 0° C. in a solution of chloride of zinc, and in a water bath drops of naphthaline were cooled to 40° C.

In these experiments the over-cooling of the drops is more easily and securely obtained the smaller their diameters, and the over-cooled drops at once solidify when touched with a fragment of the solid.

[1] *Journal de Physique*, tom. v. p. 212.

[2] Dufour, *Ann. de Chimie*, 3e, tom. lxviii. p. 370, 1863.

They also solidify when touched with a solid of different material; in this case, however, the solidification does not appear to be so certain, and the action probably arises from local agitation of the drop.

Similar over-cooling of small water drops may occur in the atmosphere, and if this happens the experiments of Dufour throw light upon the formation of hail, hoar-frost, etc., whether in the atmosphere itself or in contact with the surfaces of other bodies.

157. Fusion of Alloys.—Alloys formed of two or more metals, although they obey the general laws of fusion, possess the peculiar property of fusing at a temperature generally lower than the melting point of any of the constituent metals. Thus an alloy of 5 parts of tin and 1 part of lead fuses at 194° C., and Rose's fusible metal, which consists of 4 parts of bismuth, 1 of lead, and 1 of tin, melts at 94° C.

Similar results occur in the case of mixed salts. Thus a mixture of the chlorides of sodium and potassium fuses at a lower temperature than either constituent, and a mixture of equivalent quantities of the carbonates of sodium and potassium melts at a temperature below the fusing point of either, and is used to facilitate the fusion of certain minerals in chemical analysis.

In most cases, however, alloys melt like amorphous bodies. There is at first a general softening of the whole mass. As the temperature is raised the most fusible constituent melts first, and if it is plentiful in the alloy it liquefies the whole mass, but if it is present only in a small proportion its liquefaction only brings the mass to the pasty condition of an amalgam; so that complete liquefaction is only attained when the melting point of the less fusible constituent is reached. If the liquid substance be now gradually cooled, the temperature is found to fall till the melting point of the less fusible constituent is reached. Here it remains stationary till the solidification of this part is completed, the latent heat of liquefaction being at the same time evolved. This completed, the temperature of the now more or less pasty mass gradually falls to the melting point of the more fusible part of the alloy. Here the temperature again remains stationary till complete solidification is effected.

Rudberg,[1] to whom these observations are due, found that in the case of a mixture of lead and tin the lower fixed point remained stationary at 187°, whatever the proportions of lead and tin. The higher fixed point, on the other hand, depended on the proportion of the constituents. It approached the lower fixed point, and finally coincided with it as the composition of the alloy approached the formula $PbSn_3$, in which case there is only a single fixed point, and

[1] Rudberg, *Pogg. Ann.*, vol. xviii. p. 240; vol. xix. p. 125; and *Ann. de Chimie*, 2e, tom. xlviii. p. 353, 1831.

the fusion takes place as for a simple body. For this reason $PbSn_3$ is regarded as a *chemical* alloy. On increasing the proportion of either lead or tin the variable point of fusion reappears and attains a maximum at the fusing point of lead or tin, according as one or other is in excessive preponderance.

TABLE OF MELTING POINTS OF ALLOYS

$PbSn_5$	194°	$BiSn_3$	200°
$PbSn_4$	189	$BiSn_2$	167
$PbSn_3$	186	$BiSn$	141
$PbSn_2$	196	$PbSn_4Bi_5$	118·9
$PbSn$	241	$Pb_2Sn_3Bi_5$	100
Pb_3Sn	289	$PbSnBi_4$	94

158. Change of Volume during Fusion.—The majority of substances occupy a larger volume in the liquid than in the solid state. In general, expansion occurs during liquefaction. Several substances, however, contract on melting, a notable example being ice. In the former class the solid will sink in the liquid, and in the latter it will float.

The change of volume which accompanies the change of state from solid to liquid may be estimated by the weight thermometer (Art. 79). A known weight w_1 of the solid substance is placed in the bulb of the thermometer, and the instrument is then filled up with a weight w_2 of some liquid which has no action on the solid. By noticing the weight of liquid expelled between two chosen temperatures below the melting point, the coefficient of expansion of the solid may be obtained in the ordinary way; and similarly, by observations above the melting point, the coefficient of expansion of the same substance in the liquid state may be obtained. A curve may then be plotted, showing the relation between volume and temperature under constant pressure, both in the solid and liquid states as well as in the passage from the one state to the other. To determine the latter we require the weight w of the liquid expelled from the thermometer during fusion.

The observations of the change of volume may be made in a continuous manner by enclosing the substance in a large thermometer bulb, furnished with a graduated stem. The variation of level of the liquid in the stem indicates the manner in which the volume changes in the neighbourhood of the fusing point. This relation has been examined by G. A. Erman[1] and H. Kopp.[2]

[1] G. A. Erman, *Pogg. Ann.*, vol. ix. p. 557, 1827; *Ann. de Chimie et de Physique*, 2e, tom. xl. p. 167.

[2] H. Kopp, Liebig's *Annalen*, vol. xciii.

In the case, of ice Erman found below zero a mean coefficient of a dilatation 0·000057. The increase of volume of the ice with temperature is represented by the part AB of the curve in Fig. 63. At the point of liquefaction there is a very rapid contraction, which continues after the whole mass is liquefied, in a much smaller degree, however, till the temperature has risen to 4° C., represented by the point D. Here the density is greatest. Beyond this point the liquid at first dilates rapidly along DE, and then expands uniformly along the line EF, the mean expansion of the water here being less than that of the ice along the line AB. Kopp finds that the change of volume at zero is much more sudden than that indicated by Erman.

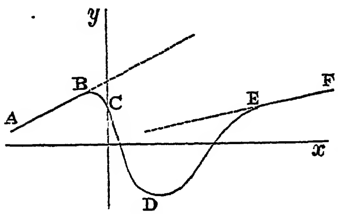


FIG. 63.—Water-substance.

In the case of phosphorus the expansion of the solid is represented by the line AB (Fig. 64), and in the liquid by the line CD. The part BC represents the change at the melting point. It has not been determined accurately, but it is probably very nearly parallel to the axis of volume. The inclinations of the lines AB and CD show that the expansion is greater in the liquid than in the solid state.

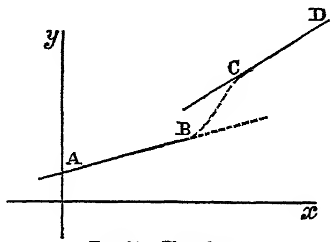


FIG. 64.—Phosphorus.

A fusible alloy, consisting of 1 part of tin, 1 of lead, and 2 of bismuth, gave a curve of great interest. The expansion of the solid is represented by the line AB, and that of liquid by FG, which is a continuation of AB, showing that the expansion of the liquid is the same as that of the solid. In the process of liquefaction the volume falls to a minimum at D, and then expands again rapidly along EF.

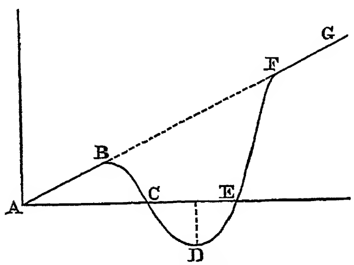


FIG. 65.—Fusible alloy.

These examples, which have been largely increased in number by Kopp, show that at the fusing point there is generally an anomalous dilatation, and that the change of volume is not always sudden, but that the curve connecting volume and temperature is in all cases probably continuous.

The force attending the expansion during change of state, especially in the solidification of water, seems to have very early attracted the attention of experimental philosophers. Boyle[1] found that water confined in a strong brass tube while it froze lifted a weight of 74 lbs. placed on the stopper, and Huygens[2] succeeded in bursting a cannon by freezing water confined in it. The Florentine academicians in the same manner burst a small brass shell, and in 1784-85 Major Williams[3] burst strong iron shells.

The expansion of water during freezing is attended by many beneficial and many destructive results in nature. Those commonly observed are the bursting of water-pipes, the raising of pavements, the bursting of plant cells, and the splitting of trees and rocks, while the general fertility of the soil is increased by the disintegration of its parts.

The expansion of water commences while it is yet a little warmer (4° C.) than the freezing point. This seems to have been first noticed by Beaumé, and is mentioned in his account of his hydrometer. De Luc and Rumford[4] also examined this point more attentively, and the latter pointed out some important consequences of this singularity in the great operations of nature.

The expansion of some substances in solidifying is taken advantage of in the manufacturing arts. Thus iron, bismuth, and antimony expand during solidification, and when cast in any mould they expand into every chink and take up its impression exactly. The contraction of phosphorus, on the other hand, prevents it adhering to the mould in which it is cast, and it is for the same reason that basaltic columns are found in nature.

159. Influence of Pressure on the Melting Point.—So far we have considered fusion and solidification under a constant pressure, and it remains now to be determined whether the melting point of a substance depends in any way upon the pressure, or if melting takes place at the same temperature whatever be the pressure to which the substance is subjected. Attention was first directed to this matter by Professor James Thomson[5] in 1849, who showed that it followed from the principles of the mechanical theory of heat that the melting point of a substance like ice, which contracts on liquefaction, should be lowered by increase of pressure, and by analogous reasoning it followed that the melting point will be raised by increase of pressure

[1] Boyle, *History of Cold*.

[2] Du Hamel, *Hist. de l'Acad. Roy.*, tom. i. p. 1, § 2, chap. i.

[3] *Edin. Phil. Trans.*, vol. ii.

[4] Count Rumford, *Essays*, vol. vii. p. 281, etc.

[5] J. Thomson, *Edin. Phil. Trans.*, Jan. 2, 1849. See also Sir Wm. Thomson's *Mathematical and Physical Papers*, vol. i. p. 156.

if the substance expands during liquefaction. Such a result might be surmised without either theoretic or experimental demonstration; for if the substance expands on fusing, then increased pressure is unfavourable to liquefaction, whereas the contrary holds if the substance contracts in passing from the solid to the liquid state.

The reasoning by which Thomson established his conclusion was exceedingly ingenious, and although faulty and incomplete in the original, it may be moulded so as to meet the full requirements of the problem. We consequently reproduce it here with the necessary amendments, for although the same results may be obtained at once from the fundamental formulæ of thermodynamics (Chap. VIII.), Thomson's mode of attack is most instructive. In the first place, let a cylinder filled with air be closed with an air-tight piston, and let the walls of the cylinder and the piston be non-conductors of heat, while the bottom of the cylinder is a perfect conductor. Now if the bottom of the cylinder be placed in contact with a mixture of ice and water, and if the piston be gradually forced down, work will be spent in compressing the air, and an equivalent quantity of heat will be generated in the air, which will pass through the conducting bottom into the mixture of ice and water. The temperature of this mixture will not be altered during the operation. A certain quantity of the ice will be melted, and the compressed air in the cylinder will finally come to the freezing point 0° C. If now the cylinder be removed from the mixture (the piston being kept fixed) and placed with its bottom in contact with the bottom of a similar cylinder containing ice-cold water, then if the air be allowed to expand gradually, external work will be done and heat will be absorbed. This must come from ice-cold water, since the walls of the cylinders and the pistons are supposed to be non-conductors, and consequently, during the expansion of the air, some of the water will be frozen. The contents of the water cylinder will thus increase in volume, and the piston which closes it will be pushed forward, doing external work if its motion be resisted. Let this resistance be applied, so that the water while freezing does external work, and let the resisting pressure gradually diminish till at the end of the process the partly frozen water is under its initial pressure (1 atm.), and its temperature is now zero. The air in the other cylinder will also be at zero; and if it now has attained its initial volume, it will also have attained its initial pressure, since its temperature is the same as when the experiment commenced. The air is now in its initial condition, while a certain quantity of heat has been communicated to the mixture of ice and water and a certain quantity of ice has been formed in the water cylinder, and a certain

Proof of J. Thomson's theorem.

amount of work has been done by the two pistons during the expansion of the air. Thus, if the work done by the air in expanding to its initial volume were equal to that done in compressing it, there would be, on the whole, a gain of work without any expenditure, viz. that done by the freezing water against the resistance applied (over and above the atmospheric pressure) during expansion. In order that this work should be performed, an equivalent quantity of heat must have disappeared, and there must be more ice formed in the water cylinder during the expansion of the air than was melted in the mixture of ice and water during the compression, and if this work is really gained we are furnished with an engine which will perform work by using up the heat of a single body, viz. that of the mixture of ice and water, and this is a violation of one of the forms of the second law of thermodynamics (p. 49). If this be impossible, the conclusion is that the work done by the air in expanding is not equal to but less than that done on it during compression, and consequently, the pressure of the air during the successive stages of expansion must have been less than during the corresponding stages of compression; but since the volume is the same in both, it follows that the temperature must be lower during expansion than during compression—that is, the temperature of the air must be below zero during the process of expansion, or the water when freezing under a pressure greater than 1 atm. must be at a temperature below zero.

Having deduced that an increase of pressure lowers the freezing point of any substance which expands on solidification, Thomson proceeded to calculate its amount from the known data for ice. He found that for this substance the theoretical lowering of the freezing point ought to be about ·0075 of a degree centigrade per atmospheric increase of pressure. From this it appears that to liquefy ice at $-1°$ C. a pressure of nearly 150 atmos. would be required.

The conclusions to which Professor James Thomson was led by theory were soon put to the test of experiment by his brother Lord Kelvin,[1] the result being a remarkably close confirmation. A strong glass cylinder, (Fig. 66) similar to Œrsted's apparatus for the compression of water, was filled with pieces of clean ice and pure water. A glass tube about a foot long and $\frac{1}{10}$ of an inch in diameter was enclosed in the water with its open end downwards to indicate the pressure by the compression of the air which it contained. A leaden ring BB was inserted about the middle of the apparatus, so as to keep free from ice that part of the thermometer-tube where the readings were expected, and

[1] Sir William Thomson, *Proc. Roy. Soc.*, Edin., 1850; *Phil. Mag.*, vol. xxxvii., 1850.

more ice was then added above the ring, the clear space being about 2 inches deep. The thermometer was enclosed in a strong glass case to protect it from the straining influence of the high pressure to which it would otherwise be exposed. The liquid used in this thermometer was sulphuric ether. This substance was chosen because its dilatation for heat is eight or nine times greater than that of mercury, and as its density is only about $\frac{1}{20}$ that of mercury, the thermometer-tube could be made large without suffering much from strain due to the weight of the liquid. For these reasons the instrument was very delicate, each division of the stem corresponding to about $\frac{1}{70}$ of a degree Fahrenheit.

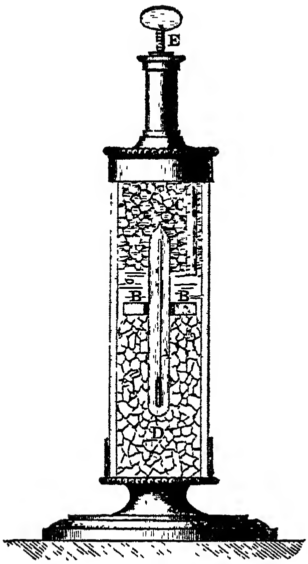


Fig 66

At the beginning of the experiment the thermometer column stood at the division 67 on the stem, and when a pressure of from 12 to 15 atmos. was applied by screwing down the piston, the reading of the thermometer rapidly descended to 61. The pressure was then suddenly removed, and the column rose again rapidly in the thermometer. The results of two experiments are given in the following table, and compared with theory on the supposition that the pressure was truly indicated by the air gauge :—

Pressure observed.	Fall of Temp. observed.	Fall of Temp. calculated.	Difference.
8·1 atm.	0°·106 F.	0°·109 F.	− 0°·003 F.
16·8 atm.	0°·232 F.	0°·227 F.	+ 0°·005 F.

More recent experiments by Professor Dewar[1] give a mean reduction of the melting point of 0°·0072 C. per atmo. increase of pressure up to 700 atmos.

It has thus been proved that if melting is accompanied by contraction the effect of increase of pressure is to lower the fusing point. The effect on substances which expand on melting was studied by

[1] Dewar, *Proc. Roy. Soc.*, vol. xxx. p. 533, 1880.

Bunsen,[1] with the simple apparatus shown in Fig. 67. The shorter arm CD contains the substance under examination, and the longer arm AB contains air which by its compression registers the pressure. The intermediate space is filled with mercury. When the temperature rises the mass of mercury expands, and the substance in the arm A is strongly compressed. By this means Bunsen found that paraffin wax, which melted at 46°·3 C. under atmospheric pressure, melted at 49°·9 C. when the pressure was raised to 100 atmos. Similarly spermaceti, which fused at 47°·7 C. under 1 atmo., had its melting point raised to 50°·9 C. by a pressure of 156 atmos. Hopkins made similar experiments on wax and stearin, and Mousson[2] by enormous pressure lowered the freezing point of water to −20° C. M. Amagat[3] has also found that C_2Cl_4 (unknown in the solid state) congeals under a pressure of 150 atmos. Other liquids were subjected to pressures ranging up to 3000 atmos., but without success.

Fig. 67.

160. Properties of Ice, Glacier Motion, and Regelation.—The lowering of the freezing point of water by pressure, or, as it may be put, the melting of ice under pressure, explains many phenomena which would otherwise be very puzzling. This melting of ice under pressure, and re-solidification when the pressure is removed, presents itself in many ordinary occurrences. The wheel-track in snow of a heavy cart is generally sheeted with a plate of clear ice. The snow, if not too cold, melts, or partially melts, under the pressure of the wheel, and solidifies again into transparent ice as soon as the pressure is removed. The same process comes into operation in the making of a snowball. If the snow is near the melting point, the pressure of the hand is sufficient to squeeze it into a compact partially-solidified mass. When the snow is squeezed between the hands, melting occurs at the points of greatest pressure, and solidification follows as soon as the resulting liquid is relieved of the pressure. If the snow be much below the freezing point, however, the pressure of the hand will not be sufficiently great, and the ball will not "make." Placed in a press, however, the snow may be squeezed into water, which, when the pressure is removed, becomes a transparent mass of ice. If snow be packed in a cylinder in which it can be strongly compressed by screwing

[1] Bunsen, *Pogg. Ann.*, vol. lxxxi. p. 562, 1850.
[2] Mousson, *Pogg. Ann.*, vol. cv. p. 161, 1858.
[3] See *Phil. Mag.*, vol. xxiv. p. 446, 1887.

forward a piston, thin rods of transparent ice will be forced through a small aperture made in the bottom of the cylinder. The snow is actually liquefied by the pressure, and solidification occurs as it escapes from the aperture. In the same way fragments of broken ice placed in a mould may be squeezed into a homogeneous mass, and ice-lenses of any shape, or masses of any shape or pattern, may be turned out like butter-prints by simply squeezing snow or ice in a mould of the required design.

Fusion under pressure.

A beautiful experiment showing the melting of ice under pressure, with solidification on relief, has been suggested by Dr. Bottomley.[1] A stout bar of ice is supported by two wooden props, one placed at each end. A wire is then looped round its middle and attached to a heavy weight, which thus hangs supported by the bar of ice. The weight causes the wire to press tightly against the ice, and, as a consequence, melting occurs under the wire. The water thus formed under the wire escapes from underneath and solidifies behind it, and, as this process continues, the wire gradually cuts its way through the ice until the weight falls upon the ground. The wire thus passes completely through the bar, but the bar is not cut in two. Reunion occurs by freezing behind the wire as fast as separation takes place by melting in front. The plane of section can be distinctly seen by means of the air bubbles which form in it, but so firmly are the two portions frozen together that breaking will take place elsewhere quite as readily as along this surface of regelation. An interesting and important process which persists throughout the whole operation is the constant flow of heat from the upper to the lower parts of any cross-section of the wire. Thus the water behind the wire is solidifying at zero, and the ice underneath the wire is melting at a lower temperature, so that the upper surface of the wire is warmer than the lower. Now we have solidification and evolution of heat above, while below there is liquefaction accompanied by absorption, and both processes are maintained in action at the same time by the flow of heat downwards from the colder to the warmer parts of the wire. For this reason it is clear that the better the conductivity of the wire the more rapid will be the flow of heat and the more quickly will the wire cut its way through the ice.

Flow of heat.

From what has been already said the gradual motion of glaciers down mountain slopes will be easily understood; but in order to make the matter quite clear, let us consider the condition of things in a very tall vertical column of snow, the temperature of the whole mass being somewhat below the freezing point. At the top we have

[1] See Tyndall's *Heat a Mode of Motion*, p. 151.

snow pure and simple, but at the bottom the pressure will be great, and if the column be tall enough, the pressure at the base will be sufficient to melt the snow. The water thus formed will escape from beneath, and being below zero will solidify as soon as free. If snow be continually added on at the top there will be continual liquefaction and after-freezing going on at the base, and a continual transformation of snow into transparent ice. Let us now consider the case of a tall block of ice. If the temperature is not too low, or if the height of the block is sufficiently great, melting will occur at the base; and if the block is situated on a hill-side, the water escaping from beneath will flow downwards, solidifying as it escapes. This is what happens on the slopes of snow-laden mountains. The snow accumulates to immense depths above the snow-line. The bottom layer liquefies under the pressure of the superincumbent mass, and a gradual slipping-away of the base occurs. The lower strata are being continually squeezed out (and on a slope this means downwards) by the pressure of the upper ones. Below the snow-line we have a stream of transparent ice gradually oozing out from underneath the snow. As the mass descends it enters warmer regions where melting occurs under a less pressure. At the points of greatest pressure melting occurs, and the stress is relieved, and the forward motion of the whole mass is effected by a continual process of alternate melting and freezing.

Glacier motion.

Regelation.

The, at first sight, peculiar property of ice known as *regelation* was first noticed by Faraday. It will now be easily understood that if two pieces of melting ice be squeezed together the pressure at the points of contact will cause melting, and the water flowing away from these points will solidify around them when free from pressure. The two pieces of ice thus become welded together. This union or regelation takes place when two pieces of ice are placed in contact under water, even under warm water, and arises from the fact that when the ice is melting its temperature is at 0° C., and a very slight pressure at any point will cause liquefaction there with subsequent freezing around it. It is also found that the plane faces of two blocks of ice firmly unite when placed together with their plane faces vertical, so that there is apparently no pressure between the faces. In this case, however, the blocks are really squeezed together to some extent; for on account of the capillary action of the film of water between the plane faces the internal pressure is less than the external, and if the blocks be free to move—for example, if they be afloat in water—they will be squeezed together, and melting with subsequent regelation will occur at the points of contact; but if they are not free to move the pressure

inside the film will be less than the atmospheric pressure, and solidification may occur if the temperature of the film does not sensibly exceed zero.

A peculiar theory of regelation and the plasticity of ice was proposed by Principal Forbes, and has obtained much favour among many of the popular expounders of science. According to this theory the surface layer of a piece of melting ice is supposed to be in a soft and plastic condition, and the harder internal core is supposed to be colder than the surface. The conclusions drawn from these assumptions do not appear to have been obtained by any sound process of reasoning, even if the truth of the assumptions be admitted. It is now more than forty years since it was proved, both by theory and experiment, that ice may be melted by pressure, and we have seen that this property at once accounts for all the phenomena of regelation in such a simple manner that any other theory must with difficulty obtain a hearing, especially if supported on doubtful and complicated hypotheses.

The causes of the motion of glaciers have from time to time been very eagerly discussed, and a perfect unity of opinion on the subject does not appear to exist even yet. This perhaps arises from the variety of phenomena attending the motion, and to different minds different phenomena may present themselves as those which most conspicuously require explanation. Thus regarded as a whole the glacier appears to move as a viscous solid,[1] the top moving faster than the bottom, and the middle faster than the sides, so that the upper layers must be continually shearing over the lower, and the middle parts over the lateral. This motion occurs in arctic as well as in temperate regions, and proceeds by night as well as by day. According to a theory propounded by Canon Mosley[2] a glacier moves downhill like any solid body simply by alternations of temperature (Art. 15). When the mass suffers a rise of temperature it expands, the motion taking place, of course, in the direction of least resistance, namely, down the bed. When the temperature falls contraction will ensue, and the backward motion, being opposed by gravity and a complete return to the original position, will not be effected, and a gradual creeping down the bed would occur. During the contraction cracks

[1] That a bar of ordinary ice yields continuously to pressure or tension, like a plastic solid, was proved by M'Connel and Kidd in 1879, and from M'Connel's later experiments (*Proc. Roy. Soc.*, vol. xlix. p. 323) it appears that a bar of ice cut from a single crystal will bend freely when the optic axis of the crystal is in the plane of bending and at right angles to the length of the bar; but when the optic axis is perpendicular to the plane of bending, the bar refuses to yield.

[2] *Phil. Mag.*, 1869 and 1870.

may be formed, and these may become filled with snow, which on the next rise of temperature will promote the further forward motion of the lower end. A sheet of lead placed on a roof creeps downwards in the same manner. This theory explains longitudinal as well as transverse crevasses; and since the surface will experience greater changes of temperature than the lower strata, it will move more rapidly.[1]

From the observations of Koch and Klocke[2] it appears that the motion of a glacier is by no means a continuous sliding down towards the valley. The motion was found to be very irregular in the morning hours, but during the afternoon a slow downward motion took place. During the night there was on the whole a backward motion.

The controversies on this subject seem to have arisen from the desire to explain all the phenomena of glacier motion by attributing them all to a single cause. It is, however, clear that several actions are in operation, and each plays a part in the motion. Thus, while the downward motion of the mass may be explained by liquefaction arising from pressure, yet there can be no doubt that ice, like every other body in nature, is to some extent viscous, and the motion therefore becomes influenced by shearing. So also variations of temperature influence the motion, and probably cause a downward creeping as well as longitudinal and lateral fissures. To attempt to explain all the phenomena by attributing them to any single action is certainly not reasonable.

Latent Heat of Fusion

161. Experimental Determination of the Latent Heat of Fusion.—The latent heat of fusion of any substance is defined as the quantity of heat required to convert unit mass of the solid at the melting point into liquid at the same temperature. Its experimental estimation may be made in several manners founded on the general methods of calorimetry. There are, however, two general methods of procedure applicable, according as the substance is liquid or solid at the ordinary temperature of the air. In the first case a weighed quantity of the liquid is placed in a freezing mixture and solidified. The solid, while at some known temperature below the freezing point, is then placed in the calorimeter, and the amount of heat absorbed by it in liquefying and rising to some known temperature above the melting point is noted. In the second case a known weight of

[1] W. R. Browne, *Proc. Roy. Soc.*, vol. xxxiv. p. 208, 1882.

[2] *Wied. Ann.*, vol. viii. p. 661, 1879; *Phil. Mag.*, 5th Series, vol. ix. p. 274, 1880.

the solid is fused, and, while it is at some known temperature above the point of fusion, is placed in the calorimeter, and the heat evolved while cooling to some temperature below the melting point is observed. The reverse operation might of course be applied in either case.

Let θ_0 be the temperature of the solid when placed in the calorimeter, θ the temperature of fusion, and θ_1 the initial and θ_2 the final temperature of the calorimeter. Then if the mass of the substance be m, and L its latent heat of fusion, s the specific heat of the solid, and s' that of the liquid, the total heat gained by the substance in rising from θ_0 to θ in the solid state, fusing at θ and then rising from θ to θ_2 in the liquid state, is obviously

$$ms(\theta-\theta_0)+m\mathrm{L}+ms'(\theta_2-\theta);$$

and if W denotes the water equivalent of the calorimeter, the heat lost by it will be

$$\mathrm{W}(\theta_1-\theta_2)+\mathrm{R},$$

where R is the radiation correction, and may be positive or negative according to the conditions of the experiment. Consequently the equation which determines L is

$$ms(\theta-\theta_0)+m\mathrm{L}+ms'(\theta_2-\theta)=\mathrm{W}(\theta_1-\theta_2)+\mathrm{R}.$$

In order to determine L from this equation the values of s and s' are required. If these are not known by previous experiments, their values may be determined simultaneously with that of L from a single experiment by noting the changes of temperature of the calorimeter while the temperature of the solid rises through a given range between θ_0 and θ, and also while the liquid rises through some interval between θ and θ_2. Or three experiments may be made, starting with different values of θ_0 and θ_1, and thus obtaining three equations similar to the above, involving the unknown quantities s, s', and L.

If the substance, on the other hand, be solid at ordinary temperatures a known quantity of it at a temperature θ_0 above the fusing point θ is placed in the calorimeter, and the final temperature θ_2 of the calorimeter will be higher than its initial temperature θ_1. The equation then becomes

$$ms'(\theta_0-\theta)+m\mathrm{L}+ms(\theta-\theta_2)=\mathrm{W}(\theta_2-\theta_1)+\mathrm{R}.$$

162. Latent Heat of Fusion of Ice.—The accurate determination of the latent heat of fusion of ice has been the subject of much skilled investigation. The method sketched above was employed by Person.[1]

[1] C. C. Person, *Ann. de Chimie*, 3e, tom. xxx. p. 73, 1850.

His calorimeter was of the ordinary form, but closed so as to prevent loss of heat by evaporation, and the stirrer was kept in constant motion by means of clockwork. The water under investigation was enclosed in a thin copper flask furnished with a thermometer which indicated its temperature. Before immersion in the calorimeter its temperature was reduced to about $-20°$ C. by means of a freezing mixture. The flask, therefore, when placed in the calorimeter contained a known weight of ice at a temperature considerably below the freezing point.

The whole observation was now divided into two parts—(1) the observation of the change of temperature of the calorimeter while the temperature of ice rose through a certain range, and (2) the observation of the final temperature of the calorimeter. The first observation gave the specific heat of ice; and this being known, the second gave its latent heat when the necessary corrections were made. In this manner Person found for ice

$$s=0\cdot504,\ L=80\cdot02,$$

the specific heat of water at $10°\cdot5$ C. being unity.

MM. De la Provostaye and Desains[1] proceeded in a somewhat different manner. Their calorimeter was of the ordinary form, and the correction for evaporation was determined by weighing and estimating the rate of evaporation within the range of temperature employed during the experiment. A fragment of ice at zero was then carefully dried and quickly immersed in the calorimeter, and the fall of temperature observed. The quantity of ice thus introduced was estimated by weighing the calorimeter before and after its introduction. The ice being at zero, its specific heat does not appear in the equation for L; and since the temperature of fusion is zero, as well as the initial temperature of the solid, we have, if θ_1 and θ_2 be the initial and final temperatures of the calorimeter,

$$mL+m\theta_2=W(\theta_1-\theta_2)+R.$$

Hence

$$L=-\theta_2+\frac{W}{m}(\theta_1-\theta_2)+\frac{R}{m}.$$

The correction R will be small, but W will be much larger than m, and it thus appears that an error in the observation of $\theta_1-\theta_2$ will be increased in the ratio W/m. Thus, if $W=10m$ an error of $\frac{1}{10}$ of a degree in the value of $\theta_1-\theta_2$ will introduce an error of a whole unit of heat in the value of L. For this reason MM. Provostaye and Desains

[1] F. de la Provostaye and P. Desains, *Ann. de Chimie*, 3e, tom. viii. p. 5, 1843.

employed a thermometer which could be depended on to $\frac{1}{100}$th of a degree. Their final result was

$$L=79 \cdot 25.$$

More recently Bunsen[1] applied his ice calorimeter (Art. 126) to the determination of the same constant. The specific gravity of ice was first measured by a species of weight thermometer, containing mercury and a known weight of water which could be frozen. The end of the stem of the thermometer dipped into a cup of mercury, so that when the ice melted mercury entered the instrument, and from the increase of weight the contraction during fusion was estimated. Bunsen thus found the density of ice to be 0·91674. This being known, a definite quantity of heat Q was imparted to the ice calorimeter and the contraction estimated. The quantity of heat Q will liquefy Q/L grammes of ice, and the known contraction v will furnish the equation for L,

$$\frac{Q}{L}\left(\frac{1}{\rho_1}-\frac{1}{\rho_0}\right)=v,$$

where ρ_1 is the density of ice and ρ_0 the density of ice-cold water. By this means Bunsen found

$$L=80 \cdot 03,$$

the mean specific heat of water between 0° and 100° C. being taken as unity.

163. Fusion of Amorphous Solids.—In the case of amorphous substances, such as glass and iron, the passage from the solid to the liquid state is gradual and not sudden as in the case of ice and other crystalline bodies which have a distinct melting point.

During this interval of transition through the viscous stages, from the hard solid to the mobile liquid, there is a continuous absorption of heat, but no sudden absorption without change of temperature. For this reason we cannot speak definitely of the latent heat of fusion of such a substance. The passage from the liquid to the solid state is continuous. One state might be regarded as differing from the other merely in the degree of viscosity. Thus solids[2] often show traces of the liquid properties, for example, in the gradual flow of pitch and the sagging of long glass rods supported horizontally. Even in the case of crystalline substances the change from the solid to the liquid state may be continuous in the

[1] Bunsen, *Pogg. Ann.*, vol. cxli.; and *Ann. de Chimie et de Physique*, 4e, tom. xxiii. p. 66, 1871.

[2] Unless we classify as solids only those substances which do not suffer plastic yielding under stress until some definite limit is reached. A fluid would then be any substance (hard or otherwise) which yields plastically in time under any stress, however small.

same manner, but exceedingly rapid. Thus, if quantities of heat be measured along the axis OY, and temperatures along OX (Fig. 47), when the substance is in the solid state, the line OA will represent the relation between the increase of temperature and the increase of heat. If the substance melts suddenly a certain quantity of heat will be absorbed without change of temperature, and this is represented by the right line AB parallel to OY. At B the fusion is completed, and the absorption of heat will again be accompanied by rise of temperature. This is represented by the line BC. If, however, the substance softens gradually, the line AB representing the change of state will not be straight, but the whole curve ABC will be continuous, as shown in

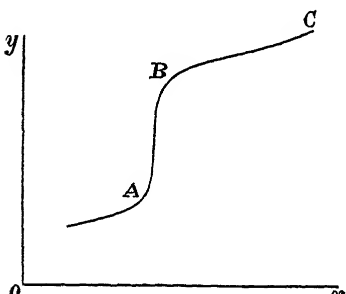


Fig. 68.

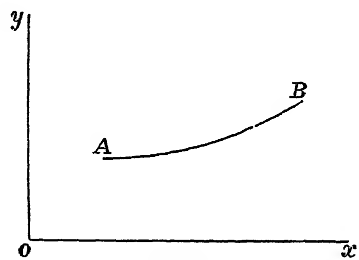


Fig. 69.

Fig. 68. The part AB will represent the stage at which there is a large absorption of heat, that is, the period of high, but not infinite, specific heat. There is here no sudden discontinuity. The change of state is merely characterised by a rapid increase in the slope and inflexion of the curve. It may even happen that a marked increase of slope does not characterise the period of change of state, but that during softening the curve, as in Fig. 69, shows no evidence of change of state. Thus the discontinuity observed in the case of water and other substances which solidify suddenly may be regarded as merely extreme cases of that exhibited in Fig. 68. In these bodies, too, the change from one state to the other may be continuous but rapid.

SECTION II

EVAPORATION AND EBULLITION

164. Molecular Motion in Liquids.—The general distinctions between solids, liquids, and gases, from the point of view of the molecular theory, have been already sketched in Art. 53. In a solid each molecule may vibrate about a position of equilibrium, but cannot move from one part to another of the mass. In a gas, on the other hand, each molecule is not only free to move throughout the mass (except in so far as it is jostled by the others), but between any two consecutive collisions its path is supposed to be straight, and the molecule is free from the action of its neighbours.

Liquids form a connecting link between the solid and gaseous states of matter. The molecules of a liquid are continually wandering through the mass, but each spends nearly all its time in collision with the others. In a gas the ratio of the time spent by any molecule in collision to that occupied in free motion is supposed to be small, but in liquids nearly all the time is spent in collisions, there is practically no free path, and each molecule is constantly under the attractive influence of those which surround it. In the interior of the liquid this influence will probably have little directive action on the motion of a molecule. Each molecule will be attracted pretty much the same in all directions, and the path travelled over by any one will depend upon its fortuitous collisions with the others.

At the surface of the liquid, however, the state of things will be very different. A molecule in this region is not equally surrounded on all sides by other molecules; so that although in the interior of the liquid a molecule may be attracted equally in all directions, and there may be no resultant molecular attraction on it, yet at the surface there will be on each molecule a resultant attraction directed towards the interior of the liquid, and along the normal to the surface. Throughout a thin surface-layer there will thus be a force on each molecule directed towards the interior. This film consequently exerts a pressure

on the liquid within, and acts like a tense elastic membrane stretched over the surface; hence the expression surface-tension.

Let us now consider a molecule in motion towards the surface. As soon as it enters the surface-layer alluded to above, a force directed towards the interior begins to act on it, so that, leaving accidental collisions out of account for the present, the motion of the molecule may be arrested and even reversed. If, however, the normal component of the velocity of the molecule be great enough, it will be able to pass completely through the surface-film, and continue its motion into the space outside the liquid. The kinetic energy of the molecule will, however, be considerably reduced by its passage through the surface-layer on account of the opposing attractive force, so that although a molecule may be in rapid motion on approaching the surface from the interior, its velocity after escape may be very small. Thus, on the whole, while some molecules escape, others are brought to rest and return into the liquid, so that the surface-film is being constantly renewed, the molecules which constitute it at any instant pass into the interior and give place to others. Those molecules which effect an escape are free to move about in the outside space, and constitute what is termed the *vapour* of the liquid, and this process of molecular escape is termed *evaporation.*

165. Evaporation in a Closed Space.—When a liquid is placed in a closed chamber (which is otherwise empty and at a uniform temperature) evaporation will take place more or less rapidly at first. After some time, however, the space outside the liquid will become partially filled with stray molecules which have escaped through the surface film. These, after escape, move about indiscriminately in the chamber, and are reflected from its walls and from each other. In this manner some, after a fitful career, will return to the liquid, and once they fall upon its surface they may be attracted into the interior. It will thus happen that a certain stage will be ultimately attained at which as many molecules will return to the liquid per second as leave it, and an equilibrium will be established. At this stage evaporation may be said to have ceased. There is no further loss to the liquid or gain to the vapour outside it; there is, however, a continual exchange going on, new molecules are being continually projected from the surface, and others are falling into it in equal number. In this case the chamber is said to be filled with saturated vapour, or the vapour is simply said to be *saturated*; while in any state before this final stage is arrived at the vapour is said to be non-saturated. A saturated vapour is thus one which is in equilibrium with its own liquid.

166. Evaporation in an Unlimited Space.—When the space into which evaporation takes place is unlimited, it is clear that when a molecule escapes from the surface it may wander about in the atmosphere and never return to the liquid. There will thus be a continual flow of molecules from the surface into the space outside, and evaporation will continue in this manner at a steady rate as long as the temperature is kept constant. The liquid will thus gradually all pass into the condition of vapour. The rate at which vapour is formed depends upon the temperature. For a given temperature it is not, however, proportional to the area of the surface of the liquid, as ordinarily supposed, but to the linear dimensions of the surface; and in an open vessel evaporation takes place more rapidly near the boundaries of the surface than at the centre. The rate of evaporation is thus not the same at all parts of the surface. This question has been examined theoretically by M. Stefan,[1] and he finds that for a circular vessel the quantity of vapour formed per second is proportional to the diameter, and, further, that the lines of flow of the vapour from the surface are hyperbolas, of which the foci are on the bounding edge of the circular surface. The surfaces of equal pressure are the orthogonal system of ellipsoids. These are nearer each other at the edge of the surface than over the centre, consequently near the edge of the vessel the vapour-pressure decreases most rapidly, and it is here therefore that the flow is greatest.

The rate of evaporation at the various parts of a free surface has been studied experimentally by A. Winkelmann,[2] and although he was unable to verify Stefan's theory very closely, he attributes the discrepancies rather to the mode of experiment than to any defect in the theory.

The rate of evaporation at a given temperature and pressure varie[s] very much with different liquids. This would of course be expected for the escape of a molecule depends on its normal velocity and th[e] nature of the surface-layer, both of which will depend upon the natur[e] of the substance. Thus a drop of ether let fall through the air disappears almost at once, a drop of alcohol less rapidly, and a drop o[f] water much less rapidly still.

From a series of experiments on the rate of evaporation of liquid[s] contained in narrow tubes, Stefan[3] was led to the law that the velocit[y]

[1] Stefan, *Journal de Phys.*, 2e série, tom. i. p. 202, 1882.

[2] *Wied. Ann.*, vols. xxxiii. xxxv., 1888.

[3] The differential equations of the motion of vapours are analogous to those [of] the potential of electric field. If a liquid evaporates in an indefinite atmosphere t[he] mass of vapour which leaves any unit of the surface per second is proportional

of evaporation varies inversely as the distance of the surface from the open end of the tube. The application of the theory of the diffusion of gases to this process led to the same law, and furnished a complete determination of the velocity of evaporation, which rendered it possible to calculate the coefficient of diffusion of vapours. These experiments have been extended by Winkelmann to several series of liquids, and have been used to determine the coefficients of diffusion of their vapours.

Similar experiments to those on evaporation may be made on the solution of solids in liquids, and the coefficient of diffusion determined.

167. Ebullition.—The rate of evaporation, depending as we have seen on the facility with which the molecules escape through the surface layer, will be favoured by anything which increases the average velocities of the liquid molecules or diminishes the surface tension. Increase of temperature has both these effects, the latter being a consequence of the former; and for this reason evaporation from a given liquid under given conditions takes place more rapidly the higher the temperature.

The effect of evaporation is to carry off those molecules of the liquid which are in most rapid motion, and consequently to diminish the temperature of the liquid. Steady evaporation carries off a steady flow of heat, so that if the temperature of the liquid is maintained constant a steady supply of heat must be given to it. Equilibrium is therefore established when the rate of supply is equal to the rate at which heat is carried away by evaporation. If the supply is considerable and the free surface small, it may be impossible for this equilibrium to be established; and as the temperature rises a point is reached at which the surface is unable to afford the means of sufficiently rapid escape to the molecules, and bubbles of vapour are formed in the interior of the liquid. At this stage the vapour-pressure is sufficient to support a bubble inside the liquid and the temperature

the electric density at this part of the surface when charged. The direction of the current of vapour is along the lines of force, and the surfaces of equal pressure are coincident with the equipotential surfaces. If a be the radius of a circular basin, k the coefficient of diffusion, P the atmospheric pressure, p' and p'' the pressure of the vapour at the surface and very far away from it respectively, the mass of vapour which escapes from the basin per unit time is

$$M = 4ka \times \frac{P - p''}{P - p'}.$$

Thus M is proportional to the radius of the basin and not to its surface, as commonly supposed (Stefan, *Trans. Vienna Acad.*, 1881, abstract in *Journal de Physique*, tom. i. p. 202, 1882).

ceases to rise. When a bubble is formed, evaporation takes place at its surface, so that the effect of the formation of such a bubble is to increase the surface through which evaporation takes place, and by this means equilibrium between loss and supply is established. Each bubble as it is formed rises to the surface, increasing in size during its ascent, and escapes into the space outside. If now the rate of supply of heat be augmented, it is found that the temperature of the liquid remains stationary. Bubbles merely form more rapidly so that the rate of loss is still maintained equal to the rate of supply of heat. The temperature at which this occurs is termed the *boiling point*, and the process of vaporisation by bubble-formation is called boiling. The temperature of boiling depends upon the pressure. The higher the pressure, the greater the difficulty of forming bubbles, and the higher the temperature at which boiling occurs. Thus the temperature of water boiling under a pressure of 760 mm. of mercury is 100° C., while under a pressure of 92 mm. boiling will occur at a temperature of 50° C., and under a pressure of 1520 mm. the temperature of boiling is 121°·4 C.

No definite law has, however, yet been discovered connecting the boiling point with the pressure, but several have been proposed. These will be considered later on. The general law of ebullition is analogous to that of fusion, viz. that a given liquid under a given pressure always boils at a definite temperature, or, in other words, the boiling point depends only on the pressure. In the case of fusion the influence of pressure is small, but the effect is decided on the boiling point. In general, when the boiling point is spoken of the temperature of boiling under the standard atmosphere (760 mm. of mercury) is meant.

The boiling point under any pressure is often defined as the temperature at which the pressure of the saturated vapour of the liquid is equal to the external pressure to which the liquid is subject. It would, however, appear much more straightforward to define the boiling point as the temperature at which boiling occurs, that is, the temperature at which a liquid gives off bubbles of its own vapour. It might then be stated as a result of experiment that at this temperature the pressure of the saturated vapour of the liquid is equal to that under which the liquid boils.

The pressure of the vapour in a rising bubble must of course be somewhat greater than the pressure outside the liquid, and even at the surface of the liquid the vapour-pressure must be a little greater than that at some distance away, for the vapour is flowing away from the surface, and it of course flows from places of higher to places of

lower pressure. The apparatus employed for fixing the boiling point on thermometers (Fig. 8) shows, however, that the pressure of the saturated vapour within the boiler is scarcely appreciably greater than that of the atmosphere outside if the escape tube be fairly wide.

168. Superheating—Variation of the Boiling Point under constant Pressure—Circumstances which determine Ebullition.—The temperature of a liquid boiling under constant pressure depends to some extent on the nature of the containing vessel. The discovery of this influence of the containing vessel is generally attributed to Gay-Lussac (1812), but as early as the middle of the last century it seems to have been generally known that the temperature of water boiling under a definite pressure was not always the same. It was found to vary within certain limits, which led to incongruities in the fixing of the boiling point on thermometers. For this reason a report on the subject was made by some of the most distinguished members of the Royal Society in 1777, in which it was recommended that the thermometer during the fixing of the boiling point should be immersed in the steam of the boiling water. From this it would appear that, even at this date, it was known that although the temperature of the liquid may depend on the nature of the vessel, or even vary with the same vessel at different times, yet the temperature of the steam was always the same under the same pressure.

As early as 1784 it was shown by Achard [1] that the boiling point of water, under constant pressure, varied much more in metallic than in glass vessels. He also noticed that if when water was boiling steadily some iron filings, or other finely-divided insoluble substance, was thrown in, the temperature of the boiling liquid was lowered 1° R. or more, and that this depression varied considerably according as the substance thrown in was powdered or in lump. The effect of soluble substances, on the other hand, was determined during the experiments of Dalton, Watt, Robison, Southern, and others on the pressure of saturated steam at various temperatures. These experiments will be considered in the next section.

The effect of dissolved air in the operation of boiling was studied by De Luc; [2] and in 1772 he propounded a theory which states in very precise terms that boiling is initiated and sustained by the bubbles of air which become disengaged from the liquid when heated. These

[1] Achard, *Nouveaux Mémoires de l'Académie Royale de Berlin*, 1785, p. 2; *Ann. de Chimie*, tom. x. p. 49. Gay-Lussac's note on the subject will be found in tom. vii. *Ann. de Chimie et de Physique*, 1817.

[2] De Luc, *Recherches sur les Modifications de l'Atmosphère, Geneva*, 1772. *Introduction à la Physique terrestre par les Fluides expansibles*, Paris, 1803.

bubbles may be seen collecting in large numbers on the sides of a glass beaker in which water is being heated. As the temperature rises evaporation takes place from the liquid into the bubble, which grows in size and rises to the surface. The part played by the air is to form a centre of evaporation, and give a start to the formation of a vapour bubble. If the liquid is quite purged from dissolved air, then according to this theory there is nothing to start bubbles in the interior, and evaporation can take place only at the free surface. In confirmation of this view De Luc found that water from which the air had been carefully expelled by boiling could be heated in a tube to a temperature of 234·5 F. without boiling.

Dissolved air.

A similar experiment showing the same effect was made by Donny[1] in 1844. Water was placed in a glass tube previously well washed out with sulphuric acid and rinsed. The water was then boiled for some time in order to expel all the dissolved air, as well as the air in the upper part of the tube. When this was effected the tube was hermetically sealed. The extremity of the tube containing the water was then placed in a bath of glycerine, the temperature of which was raised to 137° C. without ebullition of the water. At this point, however, a sudden rupture of the liquid occurred with explosive violence, projecting part of the mass to the further end of the tube. This is known as boiling by bumping. It occurs in most cases when liquids are subjected to prolonged boiling, and often leads to disastrous explosions in the case of steam-engines.

The influence of copper turnings, powdered charcoal, pounded glass, etc., in reducing the boiling point was also investigated by Gay-Lussac.[2] He considered that the boiling point depended on the nature of the surface of the containing vessel as regards its polish and conductivity for heat. Marcet,[3] on the other hand, maintained that metal turnings depressed the boiling point, because their molecular attraction for water is less than that of glass, so that the water adheres more tenaciously to the sides of the glass vessel than to those of a metallic one or to metal filings. This adhesion to the sides of the glass vessel will be influenced by dirt and impurities on the sides of the vessel, and consequently variations would be expected in the temperature of a liquid boiling in different glass vessels, or even in the same vessel at different times. When a glass flask is thoroughly washed out with sulphuric acid and rinsed with pure water, the boiling point of pure water was found

[1] Donny, *Ann. de Chimie et de Physique*, 3e, tom. xvi. 1844.

[2] Gay-Lussac, *Ann. de Chimie*, tom. lxxxii. p. 171; and *Ann. de Chimie et de Physique*, tom. vii. p. 307.

[3] Marcet, *Ann. de Chimie et de Physique*, 3e, tom. v. p. 449.

by Marcet to be 106° C. These variations were referred to molecular changes in the surface of the glass.

The theory of De Luc seems, however, to have had the most general acceptance up to the present time. The influence of dissolved air in facilitating ebullition is beyond question; but whether the action is directly due to the air itself or to particles of dust suspended in it, or to other impurities, does not seem to have been sufficiently determined. Thus M. Gernez[1] describes an experiment in which copious ebullition ensued in a liquid at the boiling point, from the surface of a small bubble of air placed in its interior, and Mr. Tomlinson[2] found that a wire gauze cage containing air might be lowered into the interior of the liquid without exciting ebullition, provided the cage and air be what he terms chemically clean. From this experiment it appeared that clean air did not cause ebullition. The specks of dust which it usually contains are the active agents.

Suspended dust.

Mr. Tomlinson's experiments on this subject are full of interest. A test tube, one third or one half full of the liquid to be examined, was placed in a warm bath and maintained at or near its boiling point, but not actually boiling. While the liquid in the tube was thus silently evaporating, its surface was touched with the end of a brass wire, and violent ebullition set in immediately. As soon as the wire was removed the boiling ceased, but it commenced again when the surface was touched with a slip of paper, or the end of an iron wire, or a glass rod. In the case of a glass rod the whole surface was active at first as the rod was passed down into the liquid. Bubbles, however, soon ceased to be given off, except at two small points. Tomlinson's explanation is that the surface became clean, and therefore inactive in separating vapour. The two specks from which vapour continued to be given off were impurities in the glass, probably iron or carbon, which were porous, or not so easily cleaned as the glass. In a tube containing ether, bubbles were rapidly discharged from two specks in the glass. Specks of this kind are often very active in separating gas from saturated solutions, such as soda-water, etc., and in setting up crystallisation in supersaturated solutions of salts.

With respect to the action of surface rugosities, the action of a rat's-tail file was examined. The surface of the hot liquid was touched with the file, and furious boiling ensued. The file was then held in the flame of a spirit-lamp, and while hot, was held in the upper part of the tube

[1] *Ann. de Chimie et de Phys.*, 5^e, tom. iv. p. 335, 1875.

[2] Charles Tomlinson, *Proc. Roy. Soc.*, vol. xvii. 1868-69, p. 240. An interesting history of the whole subject is also given by the same author, *Phil. Mag.*, vol. xxxvii. p. 161, 1869.

to cool in the vapour of the liquid, being thus sheltered from the air. The file was now found to be inactive, even though passed slowly down to the bottom of the liquid. However, when taken out and waved in the air it again became active; but when left in the liquid it soon ceased to be active, or, according to the theory, became clean.

A small pellet of writing-paper thrown into ether caused rapid ebullition for some time, the paper being tossed violently about till it suddenly sank dead and ceased to be active. A brass wire passed down to the bottom of the tube evolved bubbles from all parts of its surface, but after some time it became clean and ceased to promote ebullition, except at one point at its end, from which bubbles continued to stream off. The wire was taken out and filed, but on being inserted into the liquid again bubbles continued to stream off from two points. In the same manner a piece of flint, when dropped into methylated spirit at its boiling point, gave off bubbles in abundance all over its surface. On being taken out and broken in two it was found that when replaced in the liquid the newly-fractured surfaces were inactive, while bubbles were freely liberated at the old surfaces as before.

The behaviour of nuclei is the same in the case of supersaturated saline or gaseous solutions, and in the opinion of the author of these experiments any surface will be active or inactive in promoting evolution of gas or separation of crystals, according as it is chemically unclean or clean. A liquid at the boiling point is regarded throughout as a saturated solution of its own vapour.

While non-porous substances become inactive after some time in promoting separation of vapour, it is found that porous substances do not become inactive. Such substances, therefore, as charcoal, coke, etc., are the proper nuclei for promoting the liberation of vapour in the operations of boiling and distilling, and for preventing bumping.

Super-heating.

The possibility of superheating a liquid, as well as that of overcooling it, will depend on any circumstance which reduces the chance of the molecules at any place coming into the condition in which vaporisation or solidification may start at that place. For this reason it would be expected that very mobile liquids would be more difficult to superheat or overcool than those which are viscous. For the same reason superheating and overcooling will be more difficult the larger the quantity of liquid employed; for since it is sufficient that the required arrangement of molecules should occur at any single place for ebullition or crystallisation to set in, the probability of this happening at some place will increase with the quantity of liquid employed. Thus Dufour[1] found that drops of water suspended in a mixture of

[1] Dufour, *Ann. de Chimie et de Phys.*, 3^e série, tom. lxviii. p. 370, 1863.

oil of cloves and linseed oil could be heated much above the boiling point. Drops 10 mm. in diameter were heated to 120° C., and those which were only 1 to 3 mm. in diameter remained liquid up to a temperature of 178° C. These drops burst into vapour with a hissing noise when touched with a glass rod, or when they floated against the thermometer or the sides of the vessel. The effect of surface tension may, however, have a considerable influence in this as well as in all other cases of superheating.

When a volatile liquid is placed in a tube and cautiously heated in a bath to a temperature above its boiling point without boiling, very rapid evaporation takes place at the surface, and the cooling thus produced may be sufficient to keep the liquid at a temperature considerably below that of the bath. Thus M. Gernez[1] found that in a tube 14 mm. in diameter, containing carbon bisulphide and placed in a bath at 80° C., the temperature of the liquid in the tube did not exceed 72° C.

169. The Spheroidal State.—An apparently singular phenomenon connected with vaporisation is that known as the spheroidal state. When a drop of water is let fall on a hot metal plate the drop ordinarily boils away violently with a hissing noise. If, however, the temperature of the metal is sufficiently high, the drop does not enter into ebullition, neither does it spread over the surface and wet it as at lower temperatures, but it rolls about on the surface like a globule of mercury. The phenomenon may be easily studied by raising a metal capsule to a white heat over a bunsen flame, and dropping a globule of water carefully into the dish from a pipette. While the temperature of the dish is maintained the drop remains as if on a greased surface, while evaporation proceeds rapidly but silently from its under surface. If the lamp be removed and the dish allowed to cool, a point will be reached at which the drop comes into contact with the surface, and violent ebullition sets in with the formation of a cloud of vapour.

During the spheroidal condition it may be easily verified that the drop is out of contact with the hot metal. It is supported on a cushion of its own vapour. The eye placed on a level with the surface can easily observe through the interval between the drop (especially if it is coloured dark) and the surface any bright object, such as a flame, placed on the other side. Professor Poggendorf proved this want of contact in another manner. The two terminals of an electric battery were placed in contact, one with the drop and the other with the hot metal. While the spheroidal condition lasted no

[1] Gernez, *Ann. de Chimie et de Phys.*, 5e série, tom. iv., 1875.

current passed, but as soon as the temperature of the metal fell to the point at which boiling occurred, the galvanometer was deflected showing that contact had been established.

M. Boutigny,[1] by placing a small thermometer in the drop, found that the temperature of the drop when in the spheroidal state was always below its boiling point; and Berger[2] afterwards found that in a large globule the temperature registered by a thermometer placed in its interior marked from 96° to 98° near the bottom, and about 90° at the upper surface.

In the case of liquid sulphurous acid the temperature of the globule is low enough to freeze a drop of water placed in it. This was first shown by Boutigny, and hence the apparently extraordinary statement that water may be frozen in a red-hot crucible. The red-hot crucible has nothing to do with the freezing. It follows merely from the fact that a liquid in the spheroidal state is below its boiling point, and the boiling point of sulphurous acid is below the freezing point of water. Faraday in the same way succeeded in solidifying mercury by using solid carbonic acid instead of the sulphurous acid employed in Boutigny's experiment.

If the surface of the heated metal be flattish, so that lateral escape of the vapour is impeded, it will burst up through the centre of the drop; and it sometimes happens that when the vapour can escape laterally it issues in regular pulses, which throw the surface of the drop into beautiful undulations. As the temperature of the metal falls the vibration of the drop subsides till it becomes motionless; it then suddenly spreads over the metallic surface with a hissing noise. Contact is now established, and the spheroidal condition has terminated.

The mode of experiment may be reversed. The heated capsule may be placed afloat on the surface of a basin of hot water. While the capsule is hot it floats silently on the surface of the water supported on a cushion of vapour. According to this theory the vapour is generated so rapidly underneath that the capsule is lifted out of contact with the water in the same manner as a globule is supported on a hot surface.

The first observation of the spheroidal state is attributed to Leidenfrost, but in some of its forms it must have been known from very early times. The laundress's mode of testing the temperature of a smoothing iron by means of a drop of water is an example. A

[1] Boutigny, *Ann. de Chimie et de Phys.*, 3e série, tom. ix. p. 250; tom. xi. p. 16; tom. xxvii. p. 54; tom. xxviii. p. 178.

[2] Berger, *Pogg. Ann.*, tom. cxix. p. 594, 1863.

white hot iron may be licked with the tongue without injury, contact with the metal being prevented by the vapour developed. Similarly the hand if wet may be passed through a stream of molten metal, and solid carbonic acid may be placed in the mouth without injury. Many escapes from fiery ordeals are perhaps attributable to the same protective influence. After the hand has been moistened with ether it can be plunged into melted lead without experiencing any extreme sensation of heat.

The use of a heated metallic surface is not essential to the production of the spheroidal state. The only necessary condition is a sufficiently elevated temperature. Liquid drops may assume the spheroidal state on the surface of another liquid which is sufficiently hot; and solids such as carbonic acid snow, which vaporise without liquefaction, assume an analogous state when placed on a surface whose temperature is sufficiently high to vaporise them with the necessary rapidity.

That a liquid drop in the spheroidal state is supported on a cushion of its own vapour is confirmed by the experiment of Budde, who found that in the exhausted receiver of an air pump water assumes the spheroidal state at temperatures as low as 80° or 90° C. In this case the vapour pressure under the drop is only that necessary to the support of the drop, whereas in air the vapour pressure under the drop must support the drop and the atmospheric pressure as well.

It has been recently shown by K. S. Kristensen[1] that the heat radiated by the dish to a drop in the spheroidal state is not sufficient to account for the phenomenon, but that the heat conducted through the vapour must also be taken into account. The investigation shows that the heat conveyed in the latter manner preponderates.

170. Evaporation from Solids: Sublimation.—Of the three states of matter the liquid forms a connecting link between the solid and the gaseous. Solids when heated generally pass into the liquid, and then into the gaseous condition. Solids may, however, pass directly into the state of vapour without apparently passing through the intermediate stage—that is, solids evaporate. Ice and snow, as is well known, gradually evaporate; and in the Arctic regions this is the only manner in which evaporation can occur. Carbonic acid snow when exposed in the air rapidly passes off into gas, and can only with difficulty be liquefied in an open tube.

In these cases vaporisation occurs at the surface of the solid, and

[1] *Tidsskrift for Physik og Chimie* (2), vol. ix. p. 161; *Beiblätter der Physik*, vol. xiii. p. 155.

the process is termed sublimation. A liquid boils or passes into vapour at a temperature at which the pressure of its saturated vapour is equal to that which the liquid supports. If now the pressure of the vapour of any substance at the fusing point is equal to or greater than one atmosphere, then this substance will not exist under atmospheric pressure in the liquid state, for as soon as the solid melts the liquid will pass off into vapour. Boiling will thus, as it were, occur at the surface of the solid. This will always occur at a given temperature if the pressure is less than that of the saturated vapour of the substance at this temperature; but if the pressure be greater than this value the liquid form will be possible, and melting will occur if the given temperature is above the fusing point. Thus arsenic volatilises without melting under the atmospheric pressure, but if the pressure is increased, fusion may be effected; and Carnelley[1] showed that ice, mercuric chloride, and camphor do not melt below a certain pressure peculiar to each substance, and which he proposed to call the critical pressure.

This subject has been investigated experimentally by Professors Ramsay and Young,[2] their object being to determine if solids have definite volatilising points under different pressures just as liquids have definite boiling points. By the term volatilising is here implied a condition of the solid analogous to that of a liquid when it is said to be boiling, and not the mere passing off into vapour analogous to evaporation in liquids. The volatilising point of a solid under a given pressure is the maximum temperature at which it will remain in the solid state under that pressure. The experiments with camphor were characteristic of the whole series. Some camphor was congealed round the bulb of a thermometer which registered its temperature. The thermometer with the solid camphor thus surrounding its bulb was inserted into an air reservoir in which the pressure could be varied by means of an air pump. A tube led from the reservoir to a condenser placed in a freezing mixture. At low pressures the camphor vapour passed over into the condenser, but at somewhat higher pressures it deposited in the connecting tube, showing that at these pressures the vapour was much nearer its condensing point. When the pressure was increased to 370 mm. the camphor melted, and a liquid drop hung from the end of the solid camphor coating the thermometer; but when the pressure was again reduced to 358 mm. this drop solidified.

171. Cold produced by Evaporation—Freezing Machines.—

[1] See *Nature* for 1881 and 1882.

[2] W. Ramsay and S. Young, *Phil. Trans.*, 1884, part i. p. 37.

Evaporation is always accompanied by the disappearance of heat, and for this reason a liquid cannot continue to evaporate and at the same time maintain its temperature unless it is supplied with heat from some source. A liquid evaporating in an open vessel placed in a room at uniform temperature must therefore be at a somewhat lower temperature than the room. There is a gradual flow of heat from the room into the liquid to supply the place of that which disappears or becomes latent in evaporation. If the supply of heat be cut off while the evaporation is caused to continue, the heat necessary for the evaporation will be drawn from the liquid itself, and its temperature will fall accordingly. It is clear, therefore, that if rapid evaporation be forced by any means while the liquid at the same time is, as far as possible, prevented from receiving heat, the temperature of the liquid may be reduced to its freezing point, and solidification may be brought about as a result of the evaporation.

This was first effected in the case of water by Leslie.[1] The apparatus is shown in Fig. 70. A small capsule B containing some water is supported over a dish A filled with sulphuric acid, and the whole is placed under the receiver of an air pump. On exhausting the receiver the pressure is diminished, and as a consequence the water evaporates rapidly and begins to boil when the pressure is sufficiently reduced. The evaporation is greatly facilitated by the presence of the sulphuric acid, which absorbs the vapour almost as rapidly as it is formed. The temperature of the water is thus quickly reduced, and it ultimately solidifies, presenting the curious spectacle of a liquid freezing in the act of ebullition.

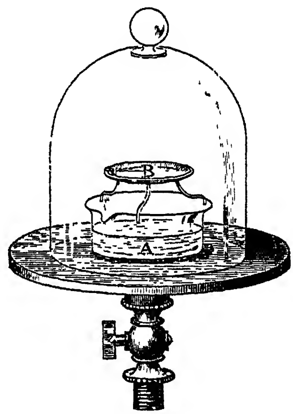


Fig. 70.

A freezing machine has been constructed by M. Carré on this principle, by which considerable quantities of water may be frozen in a short time. The water to be frozen is contained in a flask (Fig. 71), which is attached by means of a tube to a cylindrical reservoir, made of an alloy of lead and antimony, and containing strong sulphuric acid. From the farther end of the sulphuric acid chamber, a tube leads to the vertical cylinder of an air pump. A rod attached to the handle of the pump works a stirrer which keeps the acid in agitation, and by thus presenting fresh acid to the vapour hastens the

[1] Leslie, *Ann. de Chimie*, 1e, tom. lxxiii. p. 177.

evaporation. The pump is worked till freezing begins, and the acid being in constant agitation, the vapour is rapidly absorbed by it. Once freezing has commenced, the pump is worked at intervals to stir the acid. The rate of freezing depends on the strength of the acid, and when this becomes diluted it must be renewed.

Another instrument for showing the solidification of water by evaporation is Wollaston's *cryophorous* (Fig. 72), which consists of a

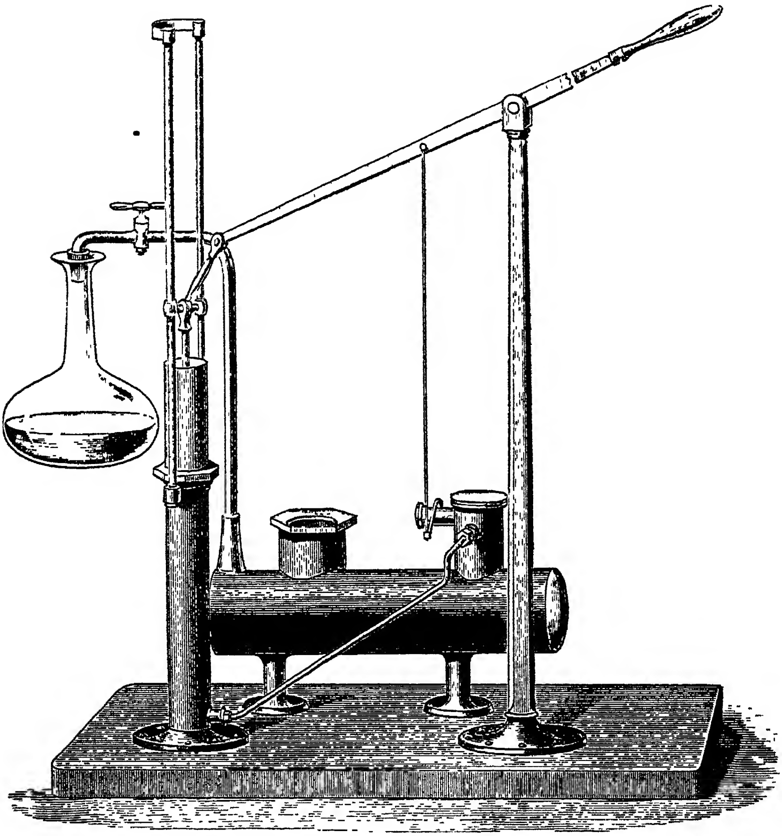


Fig. 71.

bent glass tube furnished with a bulb at each end. Some water is at first introduced and boiled, so as to expel all the air, and the apparatus is then hermetically sealed, so that it contains only water and water vapour, that is water under a small pressure at ordinary temperatures. When it is desired to solidify the water it is all placed in one of the bulbs, B, and the other bulb A is immersed in a freezing mixture. The vapour rapidly condenses in A, and is as rapidly formed in B. The

cooling produced in B by this rapid evaporation is sufficient to cause solidification of the water.

By using liquids more volatile than water, a temperature much lower than the freezing point of water may be obtained. Thus by the evaporation of sulphurous acid, which boils at $-10°$ C., or with chloride of methyl, a temperature low enough to freeze mercury may be easily obtained. By directing a jet of liquid carbonic acid on the bulb of an alcohol thermometer the reading of the instrument was reduced by Thilorier to $-100°$ C.

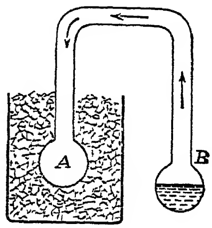
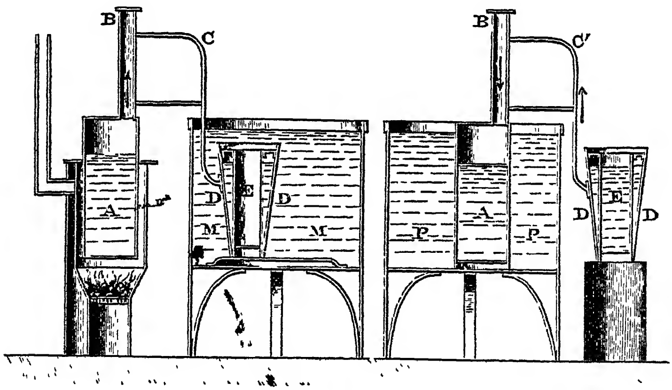


Fig. 72.

Another form of freezing machine, also manufactured by M. Carré,[1] depends upon the distillation and subsequent evaporation of ammonia. The apparatus consists of a boiler A (Fig. 73) which contains a strong solution of ammonia. This boiler is connected by a tube C to a slightly conical vessel DD called the *freezer*, and a brace binds the two firmly together. These vessels are made of strong galvanised iron plate, and can bear a pressure of 7 atms. A tubulure inserted in the upper part of the



(α) Fig. 73. (β)

boiler is filled with oil and contains a thermometer. The freezer DD consists of two concentric chambers, and it is only the space between these that the tube C communicates with. The inner chamber E receives a metal vessel containing the water to be frozen.

The process of freezing necessitates two distinct operations. (*a*) The boiler is first heated to about 130° over a furnace, while the freezer is placed in a bath of cold water. The ammonia gas is thus expelled

[1] Carré, *Comptes Rendus*, December 24, 1860.

from the solution in the boiler and condenses under its own pressure in the jacket of the freezer together with about one-tenth of its weight of water. When sufficient gas has been thus condensed, the second part (β) of the process is commenced. This consists in placing the boiler in a cold water bath, and the freezer outside covered with flannel or other non-conducting stuffs, so that it cannot receive any heat from surrounding objects. The cylinder E containing the water to be frozen is then placed in the interior chamber of the freezer. As the boiler cools the ammonia gas dissolves again in the water, and the liquid ammonia in the jacket of the freezer rapidly evaporates. During this distillation, the temperature of the freezer falls, and the water in its interior chamber is solidified. In order to secure better contact between the water cylinder and the sides of the freezer, alcohol is poured in between them. In about $1\frac{1}{4}$ hour a compact cylinder of ice is obtained. The apparatus represented in Fig. 73 gives about 4 lbs. of ice per hour at the cost of one farthing per pound. Large continuously-working forms of apparatus which produce 800 lbs. of ice per hour have, however, been built.

Latent Heat of Vaporisation

172. **Early Determinations.**—The latent heat of vaporisation of a liquid ordinarily means the quantity of heat necessary to convert one gramme of the liquid at the boiling point into saturated vapour at the same temperature and pressure.

The experimental investigation of latent heats commenced with Black and culminated in the work of Regnault. The method first employed by Black[1] was both primitive and interesting. A tin vessel containing water was set on a red-hot iron plate placed over a fire and kept at a steady temperature. The rate at which the temperature of the water rose was carefully noted, and the quantity of water in the vessel being known, this gave the quantity of heat gained by it per minute. The time was then noted from the instant the water commenced to boil till it all boiled away. This gave the quantity of heat received during complete vaporisation. The result obtained by this rough method was 450, that is the quantity of heat necessary to convert a pound of water at the boiling point under the pressure of the atmosphere into saturated vapour at the same temperature and pressure would raise the temperature of 450 pounds of water 1° C.

[1] Black, *Lectures on Chemistry*, vol. i. p. 156.

Some time afterwards Irvine,[1] at the invitation of Black, employed the method of condensation in a calorimeter, and found the number 430. Afterwards Watt, also at the request of Black, investigated the matter much more carefully, and found the number 533 for the latent heat of steam. This number is tolerably close to the best recent results, those of Regnault giving 536·5. The apparatus generally employed before the time of Regnault was similar to that shown in Fig. 74, and was not designed to give the accuracy attained by recent experimental research. The liquid was boiled in a retort C furnished with a thermometer which registered the temperature. The vapour distilled over and condensed in a spiral tube immersed in the water of a calorimeter. Two modes of procedure are now open for adoption.

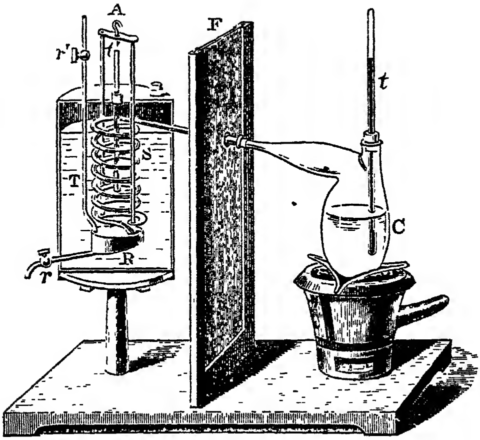


Fig. 74.

The spiral may open into a vessel situated outside the calorimeter into which the water drips as it is condensed, or the spiral may terminate in a closed reservoir R situated inside the calorimeter where the water collects and is drawn off at the termination of the experiment.

Let w be the weight of liquid arising from condensation, s its specific, and L its latent heat. Let θ be temperature of the vapour at its condensing point, θ_1 the initial, and θ_2 the final temperature of the calorimeter. The heat given out by the condensation of the weight w of the liquid will be wL, and if the liquid thus condensed be allowed to drip away from the extremity of the condensing tube into a vessel situated outside the calorimeter, the liquid first condensed will fall to θ_1, if the spiral be long enough, and that condensed at the end of the

[1] See Robison's *Mechanical Philosophy*, vol. ii., where other early determinations are cited.

experiment will fall to θ_2, so that the whole liquid condensed may be taken to have fallen to the mean temperature $\frac{1}{2}(\theta_1 + \theta_2)$ of the calorimeter during the experiment. The heat given out by this cooling of the liquid will be $ws[\theta - \frac{1}{2}(\theta_1 + \theta_2)]$. Also if W be the complete water equivalent of the calorimeter and water contained, the heat gained by the calorimeter will be $W(\theta_2 - \theta_1)$, so that if R be the radiation correction

$$wL + ws\{\theta - \tfrac{1}{2}(\theta_1 + \theta_2)\} = W(\theta_2 - \theta_1) + R.$$

If s be known, this equation gives L directly, but if s be not known, another experiment in which w is different will give us another equation containing L and s, and by means of these two equations both L and s may be determined

It is better to collect the liquid in a reservoir attached to the condensing spiral, and situated inside the calorimeter. In this case all the liquid condensed attains ultimately the final temperature of the calorimeter, so that the equation becomes

$$wL + ws(\theta - \theta_2) = W(\theta_2 - \theta_1) + R.$$

An experiment conducted with this form of apparatus is subjec[illegible] many sources of error, for the vapour in passing through the nec[illegible] the retort leading into the calorimeter may become partially conden[illegible] and arrive in the calorimeter deprived of part of its latent heat. This will lead to too small a value in the determination of L, and may be partially avoided by sloping the neck of the retort upwards, so that any liquid condensed in the neck of the retort may run back again into the boiler. Heat also passes over to the calorimeter by conduction through the connecting tube, and this increases the value of L; but there is no reason why the diminution arising from the former error should be exactly counterbalanced by the latter.

Evidently the vapour tube should be so arranged that any vapour which condenses outside the calorimeter should remain outside, and all that condenses inside should remain inside. Want of precaution in the former respect leads to too low a value of L, and in the latter too high. It is probably for this reason that Rumford obtained such a high figure as 571 for water vapour. Despretz[1] subsequently found 540, and Brix,[2] who closely discusses the sources of error, obtained the same number.

Up to the time of Regnault's work on the latent heat of water vapour it was generally admitted that the *total*[3] heat of water vapour

[1] *Ann. de Chimie*, tom. xxiv. p. 323, 1823. [2] *Pogg. Ann.*, vol. lv. p. 341.

[3] The expression "total heat" is an abbreviation for the quantity of heat required to convert unit weight of the liquid at the freezing point into saturated vapour at any other temperature.

was independent of the pressure. Watt considered it established by his experiments that the quantity of heat required to convert a given mass of water at zero into saturated vapour was the same whatever the pressure of the vapour might be, and this supposed property was known as Watt's Law. Later experiments by Clément and Desormes [1] in 1819 appeared to confirm it, so that the law became generally Watt's law.

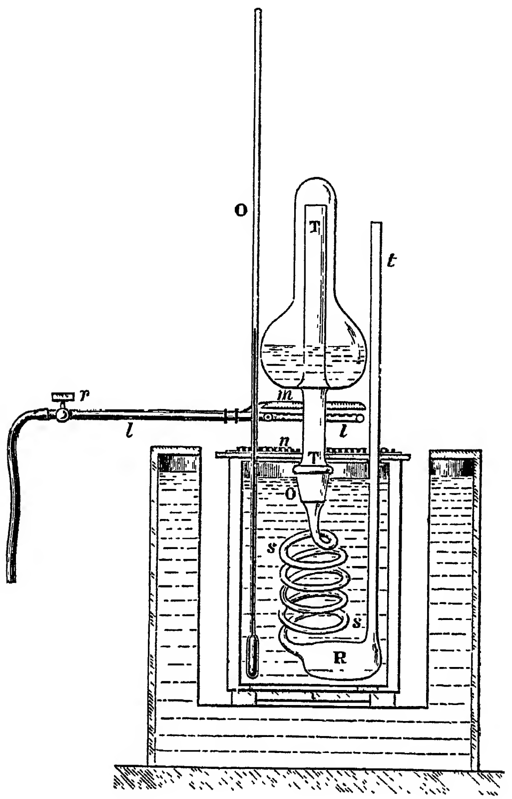


Fig. 75.

admitted on insufficient evidence, perhaps because it was very convenient in many calculations concerning the steam-engine. Several attempts were also made to deduce it theoretically.

Another law, namely, that the latent heat of vaporisation was constant, was proposed by Creighton and Southern [2] in 1803. This was known as Southern's Law.

[1] Thenard, *Traité de Chimie*, tom. i. p. 78.
[2] Robison, *Mechanical Philosophy*, vol. ii. p. 160.

That both laws are incorrect was shown subsequently by Regnault, as will appear from the account of his experiments given in Art. 175.

173. Berthelot's Apparatus.—M. Berthelot[1] has shown that many of the errors attending the early method of experimenting may be avoided by means of the apparatus shown in Fig. 75, by means of which the latent heat of a vapour may be rapidly and accurately determined without having recourse to the elaborate apparatus and precautions employed by M. Regnault. In M. Berthelot's apparatus the flask containing the liquid under examination is heated by a circular gas-burner l, burning under a metallic disc m. The centre of the flask is traversed by a wide tube TT, through which the vapour descends into the calorimeter, where it condenses in the spiral SS and collects in the reservoir R. The calorimeter is placed inside a water-jacket, and is protected from the radiation of the burner by a slab of wood covered by a sheet of wire gauze. By means of this arrangement partial condensation is avoided before the vapour enters the calorimeter, and the error arising from conductivity is corrected by observation of the motion of the thermometer placed in the calorimeter before the distillation commences and after it is completed. The weight of liquid condensed is about 20 to 30 gr. at most, and the time occupied is only from 2 to 4 minutes. By this means M. Berthelot found for the latent heat of water the value 536·2, whereas the elaborate investigation of Regnault gave 536·5. The close agreement here shows the value of the apparatus in combining speed with accuracy, and it consequently may be used to determine with sufficient precision the latent heats of rare organic liquids.

174. Method of Superheating.—The greater part of the exact investigations have been made by heating the vapour above its condensing point before it passes into the calorimeter, and in this case the specific heat of the vapour, as well as that of the liquid, appears in the equation which determines the specific heat. Let, as before, the temperature of condensation of the vapour be θ, while the initial and final temperatures of the calorimeter are θ_1 and θ_2. Let the vapour entering the calorimeter be superheated at the temperature θ', and let the specific heat of the vapour be σ. The quantity of heat given out by the vapour in cooling from θ' to its point of condensation θ is $w\sigma\,(\theta' - \theta)$, so that the equation for L becomes

$$w\sigma(\theta' - \theta) + w\mathrm{L} + ws(\theta - \theta_2) = \mathrm{W}(\theta_2 - \theta_1) + \mathrm{R},$$

supposing that the condensed liquid is all retained in the calorimeter and attains the final temperature θ_2. Three experiments in which w

[1] *Comptes Rendus*, tom. lxxxv. p. 647; and *Journal de Physique*, tom. vi. p. 337.

is varied give us three equations to determine L, σ, and s. It is here supposed that σ is constant. This is not the case with non-saturated vapours, and for the range here employed σ represents the mean specific heat of the vapour.

175. Regnault's Determination of the Latent Heat of Water

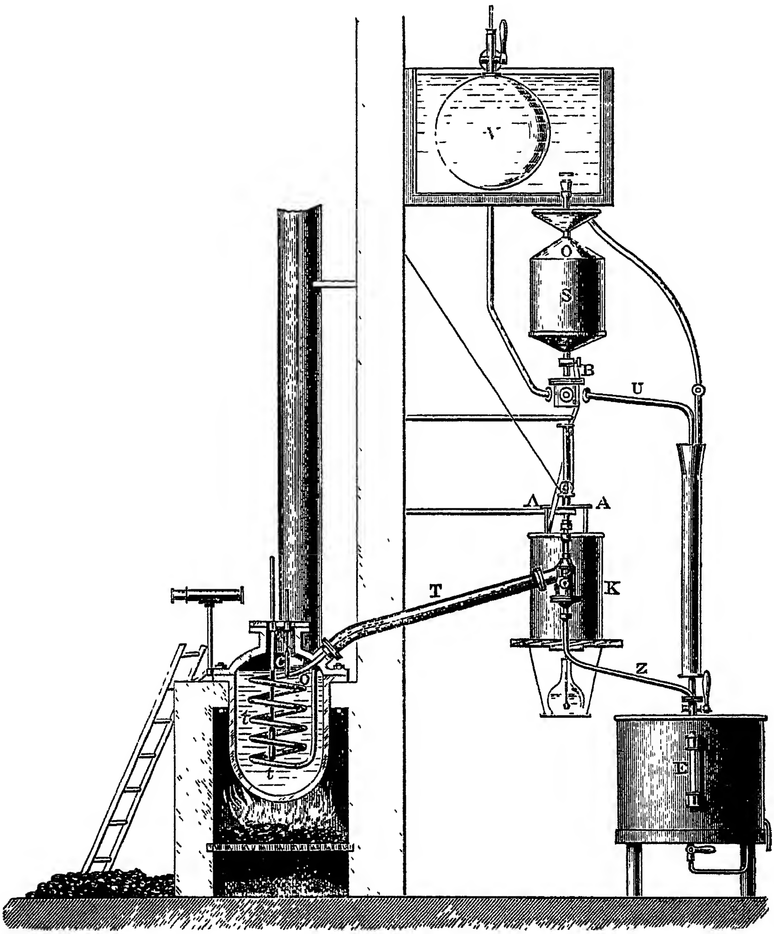


Fig 76.

Vapour.—The problem which Regnault proposed to himself was the determination of the *total heat* of saturated water vapour at divers pressures—that is, the estimation of the quantity of heat necessary to convert unit weight of water at 0° C. into saturated vapour at any pressure.

The apparatus by means of which this investigation was conducted is shown in profile in Fig. 76, and front view in Fig. 77. The vapour was generated in a strongly-made boiler (Fig. 76) of 300 litres capacity, which contained about 150 litres of pure distilled water. The vapour accumulated in the upper part of the boiler, and there entered a

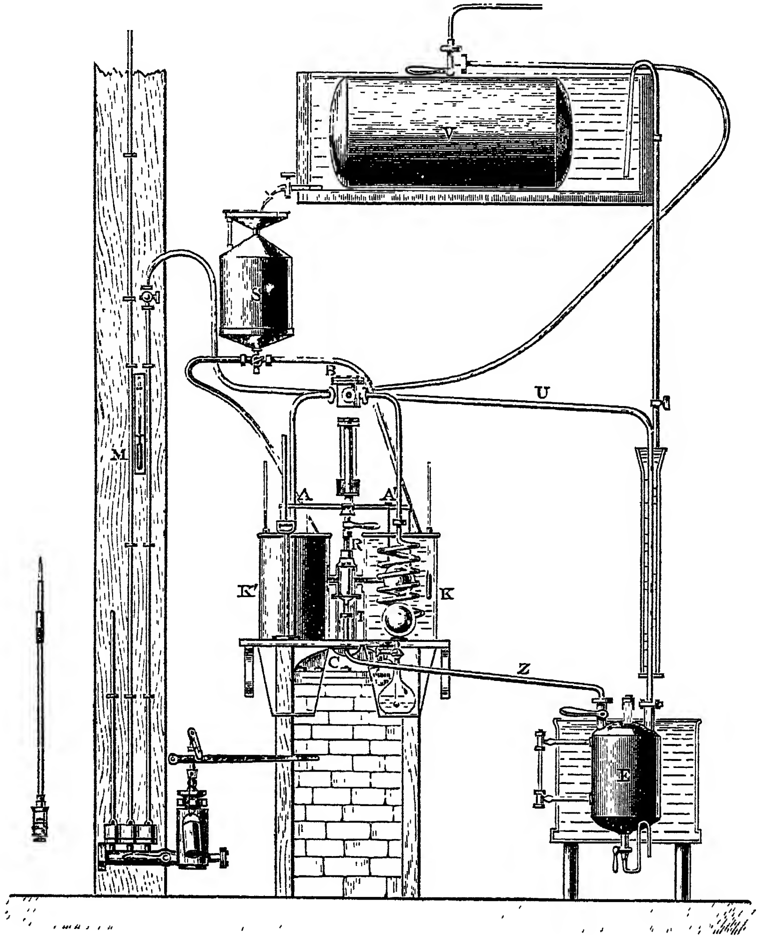


Fig. 77.

serpentine tube, enclosed within the boiler, the open end of which projected above the surface of the water. This tube carried the vapour from the boiler to the calorimeter K, and in the interval between the two, the tube was furnished with a steam jacket T, the outside of which was well wrapped in non-conducting woollen stuff. By this means the

vapour entered the calorimeter saturated, but quite dry, that is, free from mist or water-dust. The temperature of ebullition was indicated by thermometers passing down into the boiler. At high pressures the reading of the thermometer would be incorrect owing to the influence of the pressure on the bulb, and for this reason iron tubulures closed at the lower end were let into the boiler. These descended into the interior, and contained mercury in which the thermometers were placed free from all perturbations arising from the pressure of the steam.

Having arrived at the distributing piece R, the vapour could be let into either of two exactly similar calorimeters K and K′ (Fig. 77) or it could pass on into the condenser E. Immersed in each calorimeter was a condensing system consisting of two copper spheres and a spiral copper tube, as shown in Fig. 77. The vapour condensed here (when allowed to pass in), and the water resulting was drawn off in a flask and weighed.

The amount of vapour condensed during an experiment could be thus determined, and as some of the liquid adhered to the walls of the spiral and copper spheres, it was assumed that this adhesion remained constant, and therefore the water drawn off in any experiment represented the amount of condensation.

In order that the temperature of ebullition might be varied at pleasure, a large air drum V, immersed in a bath which kept its temperature constant, was connected to B, and thence with every part of the apparatus. By pumping air into (or out of) this drum the pressure in the boiler could be varied at pleasure. This pressure was measured by an open air manometer M.

In making an experiment the boiler was heated, and the steam was allowed to pass through the connecting tubes into the condenser for nearly an hour, so that the whole apparatus took up a stationary temperature, and the air was completely chased from the boiler. A preliminary experiment was made by noting for five minutes the rate of change of temperature of each of the calorimeters. The water when first placed in the calorimeter was below the temperature of the air, so that during an experiment it received heat by radiation, and also by conduction through the connecting tubes. An observation made in the same way before the boiler was heated gave the radiation correction, and this, combined with that now made after heating, gives the correction for conduction. In correcting for radiation it was found sufficiently accurate to employ Newton's law of cooling, viz. that the rate of change of temperature due to radiation is equal to the difference of temperature between the calorimeter and the air multiplied by

a constant; the value of the constant was found in this case to lie between the limits 0·001 and 0·002.

The two calorimeters were now filled with water at $\theta_1°$, and the vapour was allowed to pass into one of them till its temperature became $\theta_2°$. If w be the weight of water condensed in this operation, and W the water equivalent of the calorimeter, then the approximate equation for L is

$$wL + ws(\theta - \theta_2) = W(\theta_2 - \theta_1),$$

where θ is the temperature of condensation of the vapour—that is, the temperature of the vapour in the boiler, and s the mean specific heat of water between θ and θ_2. It is to be noted that θ_2 is not the temperature of the calorimeter at the instant the steam is shut off. During the process of condensation the temperature of the water in the condensing apparatus is above that of the calorimeter, so that after the steam is shut off the temperature of the calorimeter continues to rise for a short time to a maximum temperature $\theta_2°$. If no loss or gain of heat took place through radiation and conduction the maximum temperature would be $\theta_2 + \Sigma\delta\theta$, where $\Sigma\delta\theta$ is the sum of the corrections to be applied for all perturbating influences, and the equation for L becomes

$$wL + ws(\theta - \theta_2) = W(\theta_2 + \Sigma\delta\theta - \theta_1).$$

A similar experiment was then made with the other calorimeter. Thus when the steam was shut off from one it was turned into the other, so that while one was subject to the heating arising from the condensation of the vapour, as well as to the perturbations of radiation and conduction, the other was subject to the latter influences alone. Hence, if the two calorimeters are identical in all respects, the observations made on the variations of temperature of one can be used to determine the corrections to be applied to the other. Perfect identity could not, however, be realised, so that it became necessary to consider the corrections to be applied to each separately.

During an experiment each calorimeter was subject to two sources of error,—one due to conduction through the connecting tubes, which may be taken proportional to the difference between the temperatures of the vapour and the calorimeter, the other due to radiation and proportional to the difference of temperature of the atmosphere and the calorimeter. Denoting these differences by Δ_1 and Δ_2, the change of temperature per minute of the calorimeter due to these causes will be

$$\delta\theta = A_1\Delta_1 + A_2\Delta_2 \quad . \quad . \quad . \quad (1).$$

The coefficients A_1 and A_2 were determined by first allowing the vapour

to pass through the distributing piece R into the condenser, so that the calorimeters were heated by conduction and radiation only. Observations on the rate of change of temperature gave $\delta\theta$, Δ_1 and Δ_2 in equation (1). Another equation was formed between A_1 and A_2, with different coefficients, by allowing the vapour to pass into either calorimeter for some time, so that its temperature became elevated, and Δ_1 and Δ_2 became Δ_1' and Δ_2'. The steam was then shut out from the calorimeter and allowed to pass, as before, into the condenser, and observations were made on the rate of cooling or heating of the calorimeter. This gave

$$\delta\theta' = A_1\Delta_1' + A_2\Delta_2' \quad . \quad . \quad . \quad (2).$$

Equations (1) and (2) determine A_1 and A_2, and these being known for each calorimeter, the total correction $\Sigma\delta\theta$ to the temperature of either calorimeter during an experiment can be easily found.

By this means Regnault determined the quantity of heat

$$L + s(\theta - \theta_2)$$

necessary to convert a gramme of water at $\theta_2°$ into saturated vapour at $\theta°$, where s is the mean specific heat of water between $\theta°$ and $\theta_2°$. This is what Regnault termed the *total heat* of steam. The experiments were conducted under pressures varying from 0·22 to 13·625 atmospheres, and between these limits Regnault found that the total heat at any temperature θ was represented by the formula

$$Q = 606{\cdot}5 + 0{\cdot}305\theta.$$

In 38 experiments made under the ordinary atmospheric pressure the mean value of the total heat was found to be 637·67, the extreme values in the series being 635·6 and 638·4. Total heat of steam.

Taking the specific heat of water to be unity, the formula for the latent heat at any temperature θ will be

$$L = Q - \theta = 606{\cdot}5 - 0{\cdot}695\theta.$$

These results overthrew the laws of Watt and Southern, and settled all controversy on the subject.

When the variation of the specific heat of water is taken into account the latent heat of steam falls from 606·5 at 0° C. to 536·5 at 100° C. and to 464·3 at 200° C., and if the formula for L is quite general, it follows that the latent heat of water vapour will become zero at the temperature

$$\theta = \frac{606{\cdot}5}{0{\cdot}695} = 872 \text{ (approx.)},$$

and this consideration stands in close relation to what is known as the *continuous* passage from the liquid to the gaseous state in

the celebrated experiments of Cagniard de La Tour and Andrews (Art. 209). The critical point for water however appears to be 365° C.

176. Specific Heats of Non-Saturated Vapours.—If the vapour be superheated before entering the calorimeter, then, as we have already seen, the equation for L embraces the specific heats of the substance in both the liquid and gaseous states; so that by three experiments both these quantities as well as L may be determined. In this manner Regnault[1] found that the specific heat of superheated water vapour under constant pressure was constant within the limits of temperature employed in his experiments. The results of four series of experiments gave for steam 0·46881, 0·48111, 0·48080, 0·47963.

Regnault[2] extended his researches to several other liquids. The vapour was superheated by passing through a spiral contained in an oil bath at a temperature higher than the temperature of boiling. The heat necessary to raise the liquid to its boiling point was accurately determined, and these experiments gave both the latent heat and the specific heat of the vapour. The latter is very small compared with the former, so that the specific heat of a vapour determined in this manner is subject to all the errors of a complicated experiment. The principal results obtained by Regnault are given in the following table:—

[1] Regnault employed another method for determining the latent heats of vapours at low temperatures. A known weight of the liquid was placed in a reservoir contained in the calorimeter at a temperature $\theta_1°$, and boiling was caused by reducing the pressure in the reservoir by means of an air pump. The vapour condensed in a retort immersed in a freezing mixture of ice and sea salt. The pressure of the vapour coming from the liquid is always somewhat greater than that of the artificial atmosphere registered by the manometer. The liquid all boiled away, and the temperature of the calorimeter fell to $\theta_2°$ If $\Sigma\delta\theta$ denote the correction of θ_2 for losses of heat during the experiment, then the heat lost by the calorimeter during the vaporisation of the liquid is

$$W(\theta_1 - \theta_2 + \Sigma\delta\theta).$$

If, on the other hand, the temperature of ebullition of the liquid be θ, the heat gained by the liquid is

$$Lw + w\sigma\left(\frac{\theta_1 + \theta_2}{2} - \theta\right) - sw(\theta_1 - \theta),$$

and we have the equation

$$Lw + w\sigma[\tfrac{1}{2}(\theta_1 + \theta_2) - \theta] = sw(\theta_1 - \theta) + W(\theta_1 - \theta_2 + \Sigma\delta\theta).$$

An uncertainty occurs in the value of θ arising from the reading of the pressure of the manometer.

By the above method experiments were made at pressures varying between 13·6 mm. and 3·9 mm.

[2] *Recherches*, etc., tom. ii. p. 163.

Specific heats of superheated vapours under constant pressure (Regnault)—

Ether . . .	0·47966	Chloroform . .	0·15666
Alcohol . . .	0·45341	Acetic ether .	0·40082
Bisulphide of carbon	0·15696	Acetone . . .	0·41246
Benzine . . .	0·3754	Dutch liquid . .	0·22931
Wood spirit . .	0·45802	Ethyl chloride . .	0.27376
Essence of turpentine	0·5061	,, disulphide .	0·40081

The variation of specific heat with temperature is shown by the following table after E. Wiedemann:—[1]

Vapour.	Range of Temperature.	Specific Heat.
Chloroform . .	26·9 to 189°·8	$0·1341+0·0001354\,\theta$
Ethyl bromide . .	27·9 to 189°·5	$0·1354+0·003560\,\theta$
Benzine . . .	34·1 to 179°·5	$0·2237+0·0010228\,\theta$
Acetone . . .	26·2 to 179°·3	$0·2984+0·0007738\,\theta$
Acetic ether . .	32·9 to 188°·8	$0·2738+0·0008700\,\theta$
Ether . . .	25·4 to 188°·8	$0·3725+0·0008536\,\theta$

The specific heat of carbon dioxide is known to vary considerably near the condensing point, and it is highly probable that all other vapours vary in a similar manner in this respect.

Eilhard Wiedemann has proposed a method for determining the specific heats of vapours under constant pressure, which applies to liquids that boil between 0° and 100°. Boiling is caused at a low temperature by partial exhaustion—that is, reduction of pressure by an air pump. The vapour is then heated in a bath and allowed to pass through a calorimeter at a temperature of from 20° to 30° C., which is above the condensing point of the vapour. All the heat yielded to the calorimeter is due to the cooling of the vapour. An experiment lasts five or six minutes, and the results obtained agree with those of Regnault. They indicate that the specific heats of vapours increase notably as the temperature rises.

177. Variation of Latent Heat with Temperature.—Andrews[2] investigated latent heats for the purpose of ascertaining whether any relation existed between the latent heats and the physical properties of vapours, but he failed to deduce any fixed law. In this inquiry he was preceded by Ure, Despretz, Brix, and Favre and

[1] Eilhard Wiedemann, *Ann.*, Band ii. p. 195, 1877.

[2] Andrews, *Quarterly Journal Chem. Soc. of London*, vol. i. p. 27.

Silbermann. It has since been suggested that for different liquids [1] the latent heat multiplied by the molecular weight is approximately proportional to the absolute temperature. In other words, the molecular latent heat is proportional to the absolute temperature. Thus for water at 100° C., $\lambda = 537$, the vapour density $\delta = 9$, and $T = 373$.

$$\frac{\lambda\delta}{T} = \frac{537 \times 9}{373} = 12 \cdot 95.$$

For methyl alcohol the corresponding quantity is 12·86.

[For *internal* and *external* latent heats, see Chap. VIII. Sec. vi.]

[1] Dr. F. T. Trouton, *Phil. Mag.*, vol. xviii. p. 54, 1884; also suggested by Pictet, Ramsay, and others.

SECTION III

ON THE PRESSURE OF SATURATED VAPOURS

178. Vapour Pressure.—When a bubble of air is allowed to pass into the vacuum of a barometer tube a depression of the mercurial column is produced, which increases with the quantity of air introduced. A similar depression is produced by the vapour of a liquid, and it was in this manner that Dalton[1] first studied the pressures of saturated vapours. Small quantities of any volatile liquid may be conveniently introduced into a barometer by means of a curved pipette. If a very small globule of a liquid is allowed to ascend to the top of the mercurial column it will pass into vapour very rapidly, filling the space above the mercury, and producing a corresponding depression of the column. Another small globule will also evaporate and produce a further depression, and so on. A point is reached, however, at which further evaporation ceases, and the introduction of more liquid is not attended by an increase of vapour pressure in the space above the mercury, the temperature being supposed constant. If more liquid is introduced it merely floats on the top of the mercury (Fig. 78). Further evaporation ceases. Thus at a given temperature a definite quantity of a liquid will evaporate in a given space, and the pressure it exerts in this space is a function of the temperature only. If the space be increased, more liquid, if present, will evaporate, and if the space be reduced some of the vapour will condense. In this case the vapour (or space) is said to be saturated, and the corresponding pressure is the maximum vapour pressure for this temperature.

The behaviour of a vapour may be studied by depressing or raising the barometer tube in the cistern (Fig. 79). When the vapour is saturated the depression of the tube in the cistern merely reduces the space above the mercurial column. Some of the vapour condenses, and the height of the mercurial column remains fixed. The vapour pressure remains constant, and the glass tube slides over the column

[1] Dalton, *Memoir of the Manchester Soc.*, vol. xv. p. 409.

of mercury as if it were a bar of metal. If, however, the vapour is not saturated it behaves very nearly as a gas. Elevation of the tube increases the height of the column—that is, decreases the pressure of the vapour, and depression of the tube in the cistern increases the vapour pressure and decreases the height of the mercurial column. A non-saturated vapour nearly obeys Boyle's law.

The pressure of a saturated vapour depends on the temperature, and also on the nature of the liquid. Thus at 20° C. the depression of

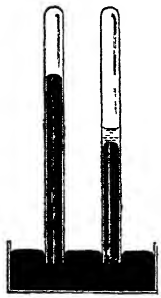


Fig 78

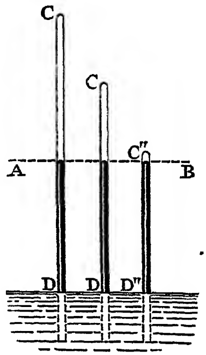


Fig. 79.

a barometer column by saturated water vapour is about 17 mm., by alcohol 60 mm., and by ether 460 mm.

If the temperature is kept constant a slight increase of pressure will produce complete condensation of a saturated vapour. If the temperature is lowered condensation occurs also, and continues till the vapour pressure reaches the maximum value corresponding to the new temperature. It is not necessary, however, to cool the whole space occupied by a saturated vapour in order to produce condensation. The cooling of any part of it will suffice. Thus, if one bulb A of a bent tube AB (Fig. 80) contains a liquid, the remainder of the tube will be filled with saturated vapour. If now B is cooled by being placed in a cold bath, or otherwise, the vapour in B will condense. The vapour pressure in B will be less than that in A, and as a consequence a current of vapour will flow from A to B. This state of things will continue as long as B is colder than A. The liquid will gradually distil into the colder part of the apparatus. The flow of vapour is accompanied by a flow of heat tending to equalise the temperatures.

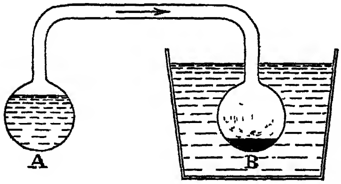


Fig. 80.

The evaporation in A is accompanied by absorption of heat, and evolution of the same takes place in B. The apparatus illustrates the action of a heat engine. The current of vapour flowing from A to B might be employed to do mechanical work (as a mill is turned by a current of water), while heat passes from a body A to another B at a lower temperature.

179. Determination of Maximum Vapour Pressures.—The first fairly accurate measurements of the pressure of saturated vapours (or maximum vapour tensions, as it is generally termed) were made by Dalton.[1] Previously the matter had been investigated by Ziegler,[2] Watt,[3] Bétancourt,[4] Southern,[5] and Schmidt,[6] in a more or less unsatisfactory manner.

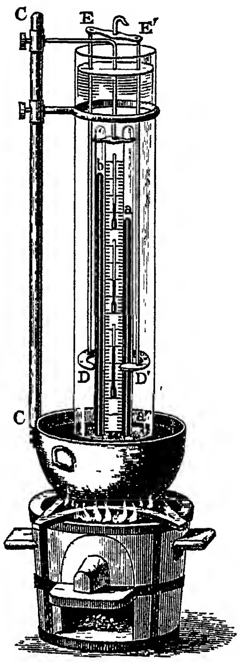


Fig. 81.

The apparatus employed by Dalton is shown in Fig. 81. Two similar barometer tubes a and b were attached to a scale which enabled the height of the mercury to be read off. Both stood in the same cistern of mercury, and were surrounded by a bath which could be heated from below, and the temperature was noted by means of three thermometers fixed along the scale, the mean of which was taken to represent the temperature of the bath. A little liquid was introduced into one of the tubes (a), and the depression of the mercurial column noted, together with the temperature of the bath. By varying the temperature the pressure of the saturated vapour was found for all temperatures within the range of the apparatus. As in this form of apparatus the temperature of the mercury is different in different experiments, it is necessary to reduce the observed depression to that which it would have been if the mercury were at zero—that is, the difference of height h must be divided by $(1 + m\theta)$, where m is the coefficient of expansion of mercury. With water vapour the pressure is equal to 1 atmo. at 100° C., and, consequently, this form of apparatus can be used only for temperatures below

[1] Dalton, *Mem. Manchester Phil. Soc.*, vol. xv. p. 409.
[2] Ziegler, *Specimen physico-chimicum de digestore Papini*, p. 48, Basel, 1759.
[3] Watt, *Robison's System of Mech. Phil.*, vol. ii. p. 29, Brewster's edition, 1814.
[4] Bétancourt, *Mémoire sur la force expansive de la vapeur*, Paris, 1792.
[5] Southern, *Robison's Mech. Phil.*, vol. ii. p. 170.
[6] Schmidt, *Journal de Physique de Gren*, tom. iv. p. 151.

100° C. At this temperature the mercury in the tube which contains the vapour will stand at the cistern level.

The chief objection to these early experiments was the want of precaution to secure uniformity of temperature in the bath. The use of several thermometers placed along the scale does not avoid this source of error. The vapour will be practically at the temperature of that part of the bath which surrounds it, and the mercury in a similar way will assume the temperature of that part of the bath around it. For accuracy the bath should be maintained throughout at the same temperature, or else some scheme should be devised by which the temperature of the vapour could be accurately known, and also that of the mercury. The pressure determined here is really the maximum pressure of the vapour in the coldest part of the tube.

The difference of height of the mercurial columns should also be measured for accuracy by means of a cathetometer; and for this purpose the use of a cylindrical glass vessel to contain the bath is objectionable as errors due to refraction are introduced. A bath chamber with a plane glass front is much superior.

Accurate determinations in which these sources of error were avoided were first made by Kaemtz.[1] He merely exposed the tubes in the atmosphere, and noted the depressions through summer and winter, the temperature ranging between −19° and +26° C. These observations were made for meteorological purposes; but a much wider range is necessary in physical investigations. The gap thus left was filled up by Regnault.

A general law connecting the vapour pressures of different substances was announced by Dalton in 1801, to the effect that the pressures of the saturated vapours of all liquids were equal at temperatures equally removed from their boiling points. This law is, however, not near the truth. Water boils at 100° C., and ether under the same pressure at 35° C., the pressure of water vapour at 80° C. (that is 20° below the boiling point) is 355 mm., while that of ether at 15° C. is 354 mm. These numbers agree excellently. In fact it was by the comparison of water and ether that Dalton deduced his rule. In the case of alcohol, however, the boiling point is 78° C., and the vapour pressure at 58° C. is only 330 mm. This is considerably too low according to Dalton's rule. Similar deviations occur with other substances.

Dühring's rule agrees much better with experiment. It is merely a modification of Dalton's law with a factor introduced depending on the

[1] Kaemtz, *Traité de Météorologie*, tom. i. p. 290.

nature of the substance. In it as we pass from temperatures of equal vapour pressure for two substances to two other temperatures of equal pressure, the differences of temperature are not taken equal, but proportional, the constant of proportionality depending on the nature of the substance.

180. Vapour Pressures at Low Temperatures.—The determination of vapour pressures at temperatures below 0° C. was conducted by Gay-Lussac[1] with a modified form of Dalton's apparatus. The vapour tube was an ordinary barometer tube CD having its upper end bent round (Fig. 82), and terminating in a pendent bulb E which could be conveniently immersed in a freezing mixture. This mixture should be fluid, so that it could be constantly stirred during an experiment. The liquid under examination was contained in the bulb, so that its temperature as well as that of its vapour was the same as that of the freezing mixture, if the temperature of the latter is kept steady for a sufficient time. Now the vapour pressure in the whole apparatus is the maximum pressure corresponding to the temperature of the coldest part—that is, the temperature of the freezing mixture. Hence the depression of the mercurial column gives the maximum pressure of the vapour at the temperature of the freezing mixture.

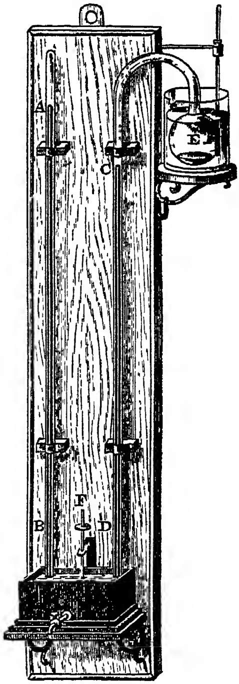


Fig. 82.

Regnault, who also employed this method, took the precaution of using a freezing mixture of chloride of calcium and snow, which is a liquid, and can be constantly stirred and kept at a uniform temperature throughout.

181. Vapour Pressures at High Temperatures.—The determination of the pressure of the saturated water vapour at temperatures above 100° C. was undertaken by a commission of the Paris Academy of Sciences in 1829 under the direction of Dulong and Arago.[2] Their experiments ranged from 100° to 224° C. corresponding to pressures varying from 1 to 24 atmospheres. The principle of the method consisted in heating a liquid in a closed boiler, and observing the temperature and corresponding pressure of the vapour.

[1] Gay-Lussac; see Biot's *Traité de Physique*, tom. i. p. 287.

[2] Dulong and Arago, *Mém. de l'Acad.*, tom. x.

The liquid was first boiled for some time to expel all the air from the boiler, which was then closed and connected with a compressed air manometer. When the liquid was heated the pressure and the temperature rose together. An observation was made by arresting the supply of heat and noting the maximum temperature attained, together with the corresponding pressure. The temperature was registered by thermometers placed in iron tubulures protruding into the interior of the boiler.

These experiments were not sufficiently numerous to furnish reliable results, and the apparatus suffered from many defects. The liquid never really entered into ebullition, so that the temperature could not be kept constant during an observation. The necessity for new determinations was soon felt, and the task was undertaken by the committee of the Franklin Institute of Pennsylvania[1] in 1830. Their apparatus, however, was little better than that of Dulong and Arago, and their two series of observations agreed neither with each other nor with those of their predecessors.

The subject was consequently taken up nearly simultaneously by Magnus[2] and Regnault[3] in 1843. The experiments of Magnus were free from the objections to which the earlier investigations were open, but they were not extended to temperatures above 115° C. The liquid was enclosed in the shorter arm of a siphon barometer which was immersed in a bath, the temperature of which could be kept constant and was determined by means of an air thermometer. The open branch of the barometer tube was connected with a free air manometer, and also with an air pump, by means of which the pressure could be varied at pleasure. The results of these experiments agree remarkably well with those of M. Regnault, whose researches were of a much more exhaustive character, extending from pressures of about 4 mm. to over 30 atmospheres.

Regnault's Experiments

182. Experiments between 0° and 50° C.—Nearly all the determinations of vapour pressures at low temperatures have been made by observation of the depression produced by the vapour in a barometer tube. The chief source of uncertainty in the method is the difficulty of knowing the exact temperature of the vapour. In Dalton's apparatus the bath extended over the whole length of the

[1] See *Ency. Brit.*, vol. xx.

[2] Gustav Magnus, *Pogg. Ann.*, vol. lxi. p. 225, 1844.

[3] Regnault, *Relation des Expériences*, tom. i. p. 467.

barometer tube, and in such a tall bath, heated from below, Regnault found that the liquid rapidly settled into layers at different temperatures as soon as stirring was stopped. Besides, in the apparatus employed by Dalton it was impossible to stir the bath without causing the mercury to oscillate in the tubes. The method in fact would only be fairly accurate for temperatures approximately the same as that of the atmosphere.

For this reason Regnault adopted a modified form of Dalton's

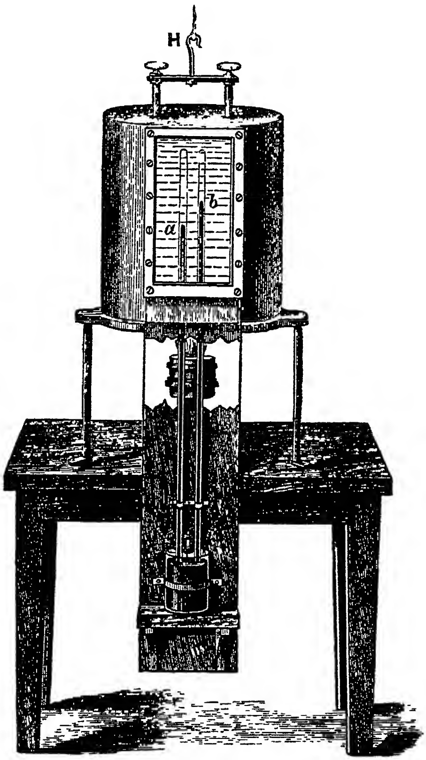


FIG. 83.

apparatus (Fig. 83) in his experiments at temperatures below 50° C. The bath was considerably shortened, but of considerable capacity (45 litres), so that it could be constantly stirred (by H) and kept at a uniform temperature throughout. The bath-chamber was furnished with a plane glass window through which the difference of level of the mercury in the tubes *a* and *b* could be read by means of a cathetometer. In order to ascertain if any error in the reading of this difference of level was caused by refraction through the glass and

liquid, a fine mark was traced on the barometer tube near the level of the mercury, and a centimetre scale was marked on the vapour tube. The difference of level between the mark on the barometer and each division of the centimetre scale on the vapour tube was then determined by means of a cathetometer—first in air, and then when the chamber was filled with water. An absolute deviation due to refraction was found, which sometimes amounted to half a millimetre, but the relative deviation—that is, the observed difference of level between any two points, one marked on each tube—was scarcely appreciable. In no case did it amount to so much as 0·1 mm.

An error in the difference of level of the mercurial columns, due to capillarity, had also to be taken into account. The surface tension in the barometer tube differs from that in the vapour tube where the mercury is in contact with a liquid or the vapour of a liquid. To determine the amount of this error two barometer tubes A and A′ were connected by a three-way tap R (Fig. 84). Dry air was admitted several times and pumped out in order to thoroughly dry the spaces above the mercury. When this had been accomplished the air was finally pumped out of both tubes, and the mercury stood at the same level in A and A′. Some liquid was then introduced into one of them (A′), and a difference of level immediately established itself, which, corrected for the weight of the floating liquid, gave the capillary correction. For water there was an elevation of the column amounting to 0·12 mm.

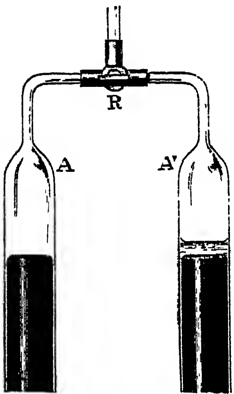


Fig. 84.

At temperatures above that of the atmosphere the temperature of the bath was maintained by a spirit-lamp applied beneath. Observations were made at intervals of eight or ten minutes, and it could thus be ascertained if slight changes of temperature were accompanied by corresponding changes of pressure, and the accuracy of the method tested. One source of error may arise in the surface of the mercury not being at the same temperature as the bath. At temperatures above that of the atmosphere the mercury in the tube outside the bath will be colder than that inside, and by conduction the upper surface of the mercury may be somewhat colder than the bath. To avoid any error from this cause Regnault always worked with the upper surface of the mercury well within the bath. When the bath is below the

temperature of the air this source of error does not present itself, for the pressure of the vapour is that corresponding to its coldest part—that is, in this case the temperature of the bath, in the former case it would be the temperature of the surface of the mercury.

In order to vary the mode of experiment and test the accuracy of the results of one method by comparison with those derived from another, Regnault modified the apparatus as follows:—The end of the vapour tube was drawn out and attached by means of a three-way joint

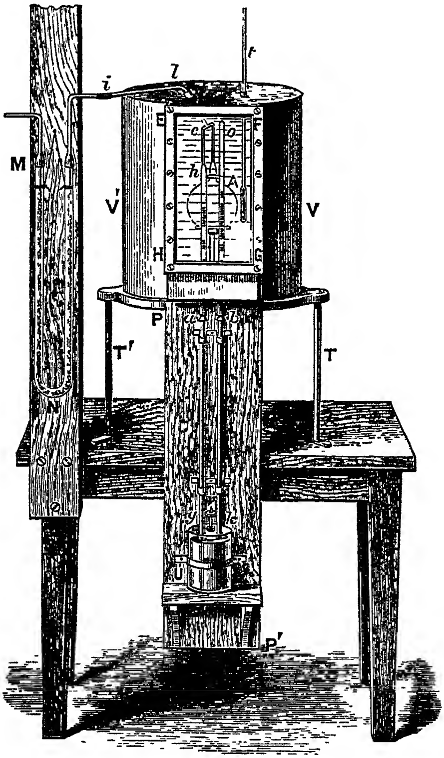


Fig. 85.

to a glass globe A of about 500 c.c. capacity. Communication was established with an air pump, as shown in Fig. 85. The globe and space above the mercury were carefully dried by admitting dry air and exhausting several times. Finally the air was pumped out, the exhaustion being carried to 1 or 2 mm.

The liquid was previously sealed up in a small glass flask or piece of glass tubing, and placed in the vapour globe A. The apparatus

being now ready, the temperature of the globe was raised till the small flask containing the liquid burst. The space *he* above the mercury became filled with vapour, and the experiment was proceeded with as before. The results of these experiments, in which vaporisation took place in the presence of a residual atmosphere of air, were in close concord with those derived by the first method of procedure in which the vaporisation took place in a vacuum.

183. Temperatures below Zero.—In determining the pressure of water vapour at temperatures below zero Regnault adopted the method of Gay-Lussac. The second form of apparatus described in the foregoing article was used. The globe containing the liquid was first immersed in melting ice, and then in a freezing mixture of crystallised chloride of calcium and snow, which was liquid, and could be kept in constant agitation. The temperature of the bath could be maintained for a short time at its lowest point by adding small quantities of snow. Observations were made at this point.

Exact determinations at low temperatures are exceedingly difficult, for here the pressure is very low and rises slowly with temperature. On the other hand, at high temperature the pressure is high, and changes considerably with a small change of temperature.

A more accurate method at low temperatures might be based on the principle of the chemical hygrometer (Art. 204), namely, by weighing the quantity of vapour contained in a large volume of saturated air. This method might be easily adopted at low temperatures in high latitudes; but in these countries where the temperature of the atmosphere is never very low, it would necessitate the adoption of specially-devised apparatus.

184. Experiments at High Temperatures.—When the pressure exceeds 300 mm. the foregoing apparatus becomes inconvenient. The length of the bath would have to be increased, and the difficulty of maintaining its temperature uniform presents itself. For this reason M. Regnault designed a new form of apparatus suitable to the determination of vapour pressures at temperatures above 50° C. The special feature of the new apparatus was the design by which the temperature of the vapour could be accurately determined, and kept constant while an observation was being made.

The liquid was placed in an air-tight copper boiler A (Fig. 86), furnished with four thermometers to register the temperature. These thermometers, which read directly to the $\frac{1}{60}$ of a degree centigrade, were not exposed directly to the vapour, but were contained in iron tubulures (Fig. 87) which were closed at their lower extremities and filled with mercury. The thermometers were thus enabled to take up

the temperature of the boiler without being subject to the pressure of the vapour which would lead to error at high temperatures. Two of

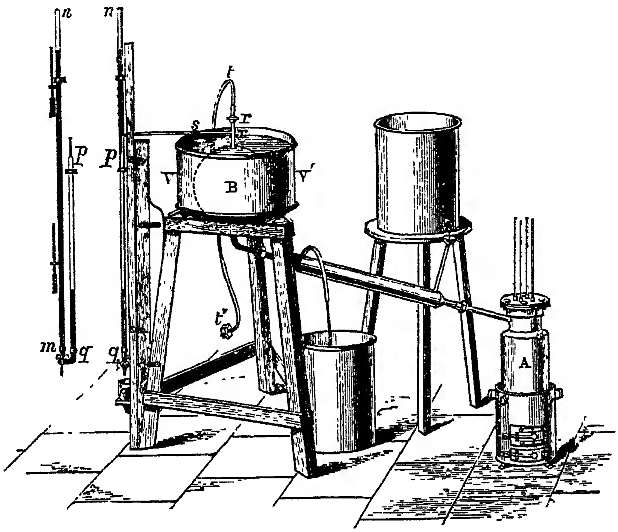


Fig. 86.

the thermometer tubes protruded into the liquid, and the other two extended only into the vapour. Regnault carefully verified that the temperature registered by the thermometers was accurately that of the vapour. A tube surrounded by a water jacket and overflow pipe led from the boiler to a large air-reservoir B (24 litres capacity), contained in a cylindrical vessel, and surrounded with water to keep it at a constant temperature. This air-reservoir was connected to a manometer pq, which indicates the pressure, and also to an air pump by means of the tube tt'. By working the pump the pressure in the reservoir could be regulated as desired, and the liquid in the boiler caused to boil under any chosen pressure. The temperature of the vapour was determined by means of the thermometers in the boiler, and the corresponding pressure of the saturated vapour of the boiling liquid was given by the manometer. The tube connecting the boiler to the air-reservoir was sloped upwards, and kept cool by the circulation of a stream of cold water. The vapour condensed in this tube, and the condensed liquid, flowed back again into the boiler. The air-reservoir was a large copper sphere surrounded by a water bath contained in a zinc vessel, so that its changes of temperature were insignificant. For pressures below one

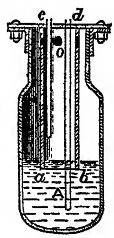


Fig. 87.

atmosphere an exhaustion pump was employed, and for higher pressures a larger and much stronger apparatus of the same description was specially built.

The facility and precision of this method are extraordinary. When the pressure is brought to any desired value steady boiling soon sets in, and the temperature remains stationary for any length of time required.

The observations were carried up to 28 atmospheres, and Regnault projected carrying them to much higher pressures with a still stronger type of apparatus and a compressed air manometer.

185. Apparatus for Volatile Liquids.—In the case of volatile liquids the vapour pressure at ordinary temperatures is considerable, and the apparatus of Art. 182 becomes inadequate to meet the requirements of the investigation. The apparatus sketched in Fig. 88 is suitable for such liquids, and was used by both Regnault and Magnus.[1] The liquid is placed in the shorter arm *a* of a siphon barometer tube, the other arm of which communicates with an air pump *p* and an open air manometer *hk*. The arm *ab* is first filled completely with mercury, and some of the liquid is then introduced above it at *c*. This liquid is then boiled, so as to expel all air from the tube. While the liquid is still hot the tube is inclined, and some of the liquid free from air is allowed to ascend to the top of the arm *a*. The remainder of the liquid at *c* is then boiled off, and dry air is admitted, the pressure of which can be regulated at pleasure by means of the air pump. This pressure is registered by means of the manometer *hk*. The apparatus now contains some liquid at *a* free from air, and is ready for experiment. The arm *ac* is now immersed in a bath, the temperature of which can be varied at pleasure, and the corresponding vapour pressure is furnished by the manometer. By sealing up the pump tube *p*, and pouring mercury into the open arm of the manometer, pressures above one atmosphere may be used.

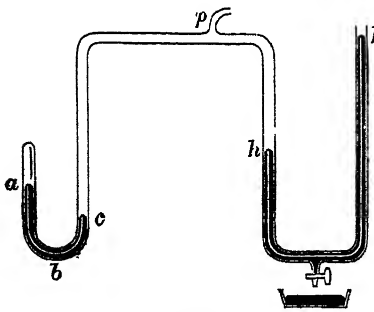


Fig. 88.

186. Apparatus for Liquefiable Gases.—A somewhat similar apparatus was employed by Regnault for the determination of the vapour pressures of liquefiable gases, such as sulphurous acid and

[1] *Pogg. Ann.*, vol. lxi. p. 226; and *Ann. de Chimie*, 3e, tom. xii. p. 69, 1844.

carbonic acid. The gas was forced into a chamber A (Fig. 89) (by a compression pump connected with the aperture P), where it liquefied under the pressure. The other chamber B was in connection with a compressed air manometer by means of the tube M. The chambers A and B were separated by a partition which descended nearly to the bottom of the vessel. The lower part of the vessel contained mercury, which could pass from A to B under the partition. The whole vessel could be placed in a bath, and kept at any desired temperature. The corresponding pressure of the vapour was determined by the manometer. In such experiments the pressures are so great that the difference of level of the mercury in A and B is negligible.

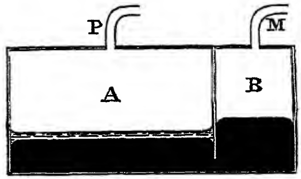


Fig. 89.

187. Vapour Pressure of a Liquid Mixture.—The pressure of the saturated vapour of a mixture of liquids was also investigated by Regnault.[1] The mixed vapours were found not to behave in general like a mixture of gases as regards pressure. Regnault distinguishes three cases—(1) When the liquids do not mix, as water and benzine. In this case the vapour pressure of the mixture is equal to the sum of the vapour pressures of the constituents. (2) When the liquids mix partially or dissolve each other to a limited extent, like water and ether. In this case the vapour pressure of the mixture is less than the sum of the pressures of the constituents, or even less than that of one of them. Thus Regnault found—

Temperature.	Water Vap. Press.	Ether.	Mixture.
15°·56 C.	13·16 mm.	361·4 mm.	362·95 mm.
33°·08	27·58 ,,	711·6 ,,	710·02 ,,

(3) The third case is that in which the liquids mix in all proportions. In this case the diminution of the vapour pressure of the mixture is still more marked.

According to the experiments of Wüllner[2] the vapour pressure of any given mixture bears a constant ratio to the sum of the vapour pressures of the constituents, at least when the liquids are mixed in

[1] Regnault, *Comptes Rendus*, tom. xxxix., 1854; *et Mémoires de l'Acad.*, tom. xxvi.
[2] *Pogg. Ann.*, Band cxxix. p. 353, 1866.

nearly equal proportions. For other proportions the law is not quite exact.

188. Empirical Formulæ.—If the pressure of a saturated vapour depends only on the temperature, some general relation between the pressure and the temperature, such as

$$p=f(\theta),$$

must exist. The form of the function will probably depend on the nature of the substance; but no general law has yet been found. The first attempt in this direction was made by Dalton, who proposed the simple law that the vapour pressure increases in geometrical progression as the temperature increases in arithmetical. This assumes that the relation between the pressure and temperature is of the form

$$p=a\alpha^{\theta},$$

or

$$\log p=b\theta+c.$$

This formula, however, holds only for small limits of temperature near the point at which the constants are determined.

Young[1] proposed a more general formula including three constants, viz.

$$p=(a+b\theta)^{m},$$

where the constants a, b, m are to be determined by means of three experiments.

Another formula suggested by Roche,[2] from theoretical considerations, belongs to the general type

$$p=a\alpha^{\frac{\theta}{m+n\theta}},$$

[1] Young, *Nat. Phil.*, vol. ii. p. 400.

Young's formula was adopted by several physicists, notably Creighton, Southern, Tredgold, and Coriolis. The form given by Tredgold (*Traité des machines à vapeur*, p. 101, 1828) was

$$\frac{p}{10}=\left(\frac{\theta+75}{85}\right)^{6},$$

while that used by Coriolis (*Du calcul de l'effet des machines*, p. 58, 1829) was

$$\frac{p}{760}=\left(\frac{1+0\cdot018780\theta}{2\cdot878}\right)^{5\cdot355},$$

and the form given by Dulong (*Mém. de l'Institut*, tom. x. p. 230) was

$$\frac{p}{760}=\left[1+0\cdot7153\left(\frac{\theta-100}{100}\right)\right]^{5},$$

which holds fairly well for water vapour up to 24 atmospheres.

[2] Roche; see Dulong and Arago's Memoir, *Mém. de l'Institut*, tom. x. p. 227.

where a, α, m, and n are constants to be determined by experiment, and θ is the temperature measured from any arbitrarily chosen zero.

Roche's form was

$$\frac{p}{760}=10^{\frac{0\cdot1644(\theta-100)}{1+0\cdot03(\theta-100)}},$$

and this was modified by Magnus [1] as follows—

$$p=4\cdot525\cdot10^{\frac{7\cdot4475\theta}{234\cdot69+\theta}}.$$

Finally, a more general formula was suggested by Biot,[2] viz.

$$\log p=a+b\alpha^{\theta}+c\beta^{\theta},$$

where a, b, c, α, β are determined by means of five experiments, and θ is the temperature measured from any chosen zero—say the lowest of the five experiments used to determine the constants.

Regnault found that Young's formula might be used to represent the results of experiments within a limited range, but that beyond these limits it had to be abandoned.

The formula of Roche,[3] however, which he used in the form

$$p=a\alpha^{\frac{\theta+20}{1+m(\theta+20)}}$$

represented the whole series of experiments with considerable accuracy, but not quite so generally and precisely as the more general formula of Biot. Writing this in the form

$$\log p=a-b\alpha^{\theta+20}-c\beta^{\theta+20}$$

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[1] Magnus, *Pogg. Ann.*, vol. lxi.; and *Ann. de Chimie et de Phys.*, 3^e, tom. xii. p. 69.

[2] Biot, *Connaissance des Temps*, 1844. The more general form would be

$$p=a\alpha^{\theta}+b\beta^{\theta}+c\gamma^{\theta}+d\delta^{\theta}+, \text{ etc.},$$

where θ is measured from any chosen zero.

[3] Roche's formula has been deduced from theoretic considerations which are open to serious objection. See Clapeyron (*Journal de l'École Polytechnique*, tom. xiv. p. 153), August (*Pogg. Ann.*, vol. xiii. p. 122; and vol. lviii. p. 334), de Wrede (*Pogg. Ann.*, vol. liii. p. 225), Holtzmann (*Pogg. Ann. Erganzungsheft*, vol. ii. p. 183). If a curve be plotted having p and θ in the formula for co-ordinates, it will have two branches. If $\alpha>1$, one of these branches (that which represents the vapour pressures) stops at the point

$$\theta=-\frac{m'}{n},$$

Regnault found

$$a=6{\cdot}2640348,$$
$$\log b=0{\cdot}1397743, \qquad \log \alpha=\bar{1}{\cdot}994049292,$$
$$\log c=0{\cdot}6924351, \qquad \log \beta=\bar{1}{\cdot}998343862.$$

In the course of a series of investigations founded on a particular hypothesis respecting the molecular constitution of matter, Rankine[1] arrived at the formula

$$\log p=\alpha-\frac{\beta}{\Theta}-\frac{\gamma}{\Theta^2},$$

where Θ is the absolute temperature. This formula, according to Rankine, represents the whole series of Regnault's experiments from $-30°$ C. to $+230°$ C. The values of the constants determined from three experiments were, for water vapour

$$\alpha=7{\cdot}831247, \quad \log \beta=3{\cdot}1851091, \quad \log \gamma=5{\cdot}0827176.$$

Rankine also proposed the equation

$$pv^{\frac{17}{16}}=\text{constant}$$

for the steam-line of water substance, v being the specific volume of the saturated vapour.

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where $p=0$. The curve here touches the axis of temperature. It has a point of inflection for

$$\theta=\frac{m(\log a-2n)}{2n^2}, \qquad p=a\alpha\frac{\log a-2n}{2n[n+m(\log a-2n)]}.$$

Finally, it is asymptotic to a line parallel to the axis of temperature given by the equation

$$p=a^{\frac{1}{n}}.$$

This is the maximum value of the pressure.

The other branch of the curve does not refer to the question. It is asymptotic to the right line $\theta=-m/n$ parallel to the axis of pressure.

[1] Rankine, *Edinburgh New Phil. Journal*, July 1849.

SECTION IV

VAPOUR DENSITIES

189. Definition of Vapour Density.—The density of any substance generally means its weight per unit volume, taken at some standard pressure and temperature. The specific gravity of a substance, on the other hand, is expressed by the ratio of the weight of any volume of the substance to the weight, under given conditions, of an equal volume of some standard substance chosen for the sake of reference. The standard substance usually chosen is water, so that the specific gravity, or specific density, of a substance is its density compared with that of water. Now if the weight of unit volume of the standard substance (water at 4° C.) be taken as the unit of weight, then the density of this substance will be unity, and the density of any other substance will be expressed by the same number as its specific gravity. This plan is adopted in the C. G. S. system, in which the unit of weight (1 gramme) is taken as the weight of a cubic centimetre of water at 4° C.

What is generally spoken of as the density of a vapour is the weight of any volume under given conditions of temperature and pressure, compared with the weight of an equal volume of dry air under the same conditions. This, then, is not the density of the vapour, in the correct sense of the word, but rather its specific gravity —air at the same pressure and temperature being taken as the standard of comparison.

Let w be the weight of a volume v of vapour at a pressure p and temperature Θ. Let w_0 be the weight of air per unit volume at 0° C., and a pressure of 760 mm. Then the weight of a volume v of air at temperature Θ and pressure p is

$$w' = w_0 v \frac{p}{760} \cdot \frac{273}{\Theta}.$$

Consequently by definition the vapour density is

$$\rho=\frac{w}{w'}=\frac{w}{w_0 v}\cdot\frac{760}{p}\cdot\frac{\Theta}{273}\quad\ldots\ldots\ (1),$$

where $w_0 = 0{\cdot}001293187$ gramme per cubic centimetre. Hence in order to measure ρ we require the volume, temperature, and pressure of a known weight of the vapour.

The result of a single experiment furnishes the vapour density at the temperature and pressure under which the experiment was made. If the vapour obeys the laws of Boyle and Charles (or rather obeys them to the same extent as air does), then the vapour density thus determined will always be the same whatever the pressure and temperature. For in this case we will have $pv = R\Theta$ in the equation for ρ, and consequently

$$\rho=\frac{w}{w_0}\cdot\frac{760}{273R}$$

which is independent of pressure and temperature.

If, therefore, it were found by experiment that ρ remains constant as the pressure and temperature are varied, we should conclude that vapours up to their point of saturation obey the laws of perfect gases. It is found, however, that this is by no means the case. As a vapour approaches its point of condensation, its density, as defined above, increases. That is, for a given increase of pressure there is a greater diminution of volume, at constant temperature, than if Boyle's law were obeyed. In other words, the product pv is not constant at constant temperature, but diminishes as the pressure increases.

No perfectly general and accurate law connecting the pressure, volume, and temperature of a vapour, or gas, up to its condensing point has yet been discovered. Sufficient experimental work has not been executed in this department to lead to the deduction of any law possessing complete generality. Several formulæ have however been proposed which apply to the fluid state with more or less precision. These will be considered later on (Section VII.). Up to the time of the experiments of Fairbairn and Tate (1860) no direct observations of vapour densities at the point of saturation had been made. The method previously employed consisted in making an observation of the density at some definite temperature and pressure, and deducing the density at all other temperatures and pressures (even that of saturation) on the supposition that the vapour obeyed Boyle's law. This method, though obviously inaccurate, is practised in most ordinary work up to the present day; we shall, therefore, describe

some of the methods which have been employed in the investigation of vapour densities.

190. Gay-Lussac's Method.—The method employed by Gay-Lussac[1] was exceedingly simple, and specially suitable for the measurement of the vapour densities of volatile liquids. For liquids, however, which have a high boiling point the method fails. The apparatus is shown in Fig. 90, and although it has been superseded by more accurate forms it sufficiently illustrates the principle of the method. It consists of an iron dish containing mercury in which a tall graduated glass tube AB filled with mercury is inverted barometer-wise. This tube is surrounded by a glass cylinder open at both ends, which is filled with water, and can be heated so as to keep the inner tube at a fairly fixed temperature. The apparatus being ready for experiment, a weighed quantity of the liquid under investigation is sealed up in a small glass bulb, or placed in a small stoppered phial, which is slipped under the mouth of the inner tube. When let go it rises through the mercury to the top of the tube, where, under the diminished pressure and increased temperature, it bursts, and the liquid is all vaporised if the temperature is sufficiently high, or the space above the mercury sufficiently large. This being secured, the volume occupied by the vapour is read off by means of the graduations on the tube, and the pressure is determined by measuring the difference of level between the mercury in the tube and cistern.

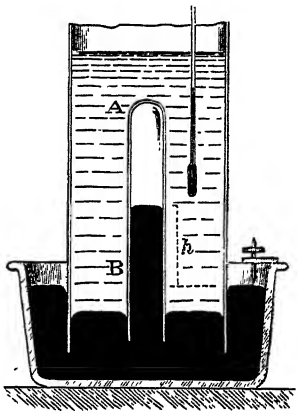


Fig. 90.

The temperature is taken as that of the bath, which should be constantly stirred to secure uniformity. Stirring, however, will cause oscillation of the mercurial columns since the water rests on the mercury, and for that reason the apparatus is open to the same objection as that of Dalton for determining the pressures of saturated vapours. The difference of level between the surfaces of the mercury in the tube and cistern is determined by means of a cathetometer, and a vertical screw pointed at both ends. The length of this screw is accurately determined, and the lower end is placed in contact with the surface of the mercury in the cistern. The difference of level between the surface of the mercury in the tube and the upper end of

[1] Gay-Lussac, *Ann. de Chimie*, 1e, tom. lxxx. p. 218, 1811.

the screw is determined by means of a cathetometer, and this, added to the length of the screw, gives the elevation of the mercury in the tube over that in the cistern. This column corrected for temperature and subtracted from the height of the barometer, also corrected for temperature, gives the pressure of the vapour.

The pressure, volume, and temperature of the vapour being thus known as well as its weight, the density is found by means of the formula of Art. 189—

$$\rho = \frac{760 w \Theta}{0{\cdot}001293 \times 273 pv}.$$

By varying the temperature of the bath or the quantity of liquid, the vapour density at different stages approaching the point of saturation may be determined, and a comparison of the results will indicate the extent and nature of the departure from Boyle's law. At high temperatures, however, the tension of the mercury vapour becomes considerable, and this method becomes inapplicable.

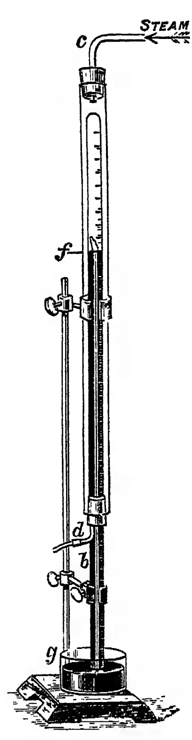


Fig 91.

The apparatus of Gay-Lussac has been modified and improved by Hofmann. In the new form (Fig. 91) the vapour tube is about 1 metre long, so that the vapour is contained in the vacuum of a barometer tube. The water bath is replaced by a steam jacket (*cd*), so that a constant definite temperature may be maintained. The liquid is enclosed in a very small stoppered bottle which rises to the surface of the mercury, and under the diminished pressure the stopper is ejected and the liquid evaporates. Other vapours than water may be used in the vapour jacket, or the water may be boiled at other pressures than that of the atmosphere, by attaching the tube *d* to an air pump by means of which the pressure inside the jacket may be varied, and different definite temperatures are thus at our disposal. Since in this form the liquid evaporates in a torricellian vacuum, the vapour is formed under a much lower pressure than in Gay-Lussac's apparatus, so that the vapour density of a liquid which boils in air, say at 150° C., may be determined by use of the steam jacket. This is of great importance in the case of those substances which decompose at their boiling point under ordinary atmospheric pressure.

191. Regnault's Investigations.—The principle of the method employed by Regnault[1] in his study of vapour densities was the same as that of Gay-Lussac, but the apparatus was different in several respects, being similar to that used in his experiments on the pressure of saturated vapours (Fig. 85). A weighed quantity of the liquid was sealed up in a small bulb, and placed in the globe of the vapour chamber. The barometer tube was dispensed with, and the vapour tube was attached at its lower end to another vertical tube, open at its upper end, so that the two tubes thus joined formed the two branches of an open air manometer. The surface of the mercury was always kept at a constant level in the vapour tube, so that the apparent volume of the vapour was always the same.

This volume being accurately known at one temperature, the volume at any other temperature is easily deduced from the known coefficient of expansion of glass. The weight of liquid was previously determined, so that it could be completely vaporised in this space at the temperatures employed. The pressure due to the residual air left in the apparatus was accurately determined before the vaporisation of the liquid, and this, corrected for change of temperature and subtracted from the pressure indicated by the apparatus, gave the pressure of the vapour. Being thus furnished with the pressure, volume, temperature, and weight of the vapour, its density may be determined as above.

The advantage of this form of apparatus over Gay-Lussac's lies in the structure of the bath, which could be constantly agitated and maintained at a uniform temperature throughout without disturbing the mercury.

Regnault's first series of experiments related to the density of water vapour at 100° C., and under pressures not greater than half an atmosphere. Within these limits he found that Boyle's law was very closely obeyed.

The second series of experiments investigated water vapour under feeble pressures and near the ordinary temperature of the air. From this series he concluded that Boyle's law might be applied up to a saturation fraction 0·8. The departure from the law after this point he thought might be due to anomalous condensation arising probably from contact with the walls of the vapour chamber.

The third series dealt with the density of water vapour in air at its saturation point between 0° and 25° C., the conclusion being that Boyle's law was obeyed up to the point of condensation without very serious error.

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. xv. p. 141, 1845.

192. Mayer's Method.—The method designed by Victor Mayer depends on an ingenious device for measuring the volume of the vapour. The apparatus is shown in Fig. 92. It consists of a cylindrical bulb B furnished with a long narrow stem, from which a fine tube branches off near the top and dips under the surface of a basin of mercury. Immediately over the end of this branch tube a graduated glass D tube filled with mercury is inverted barometer-wise in the basin of mercury.

In making an experiment, the bulb B is heated by immersion in a bath to the temperature at which it is desired to make the experiment. During this operation the air within the bulb expands, and may be allowed to escape into the air through the side branch, over the end of which the tube D has not yet been inverted. When B has attained its stationary temperature the graduated tube D is inverted over the end of the branch, and a small flask containing a known weight of the liquid under investigation is quickly introduced into B through the stoppered end C of the stem.

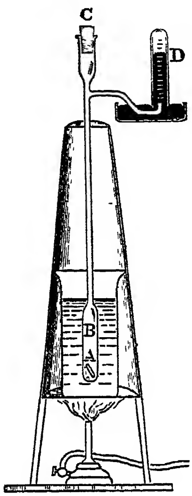


Fig. 92.

The temperature of the bulb being well above the boiling point of the liquid, the contents of the flask are vaporised at once, and the vapour thus quickly formed pushes the air before it through the side tube, whence it rises through the mercury into the graduated tube D. When equilibrium is attained a certain mass of air has been expelled which can be determined by observing its volume, temperature, and pressure in the tube D. The result of the whole process is that the space previously occupied by this mass of air in the bulb is now occupied by a known mass of vapour at the same temperature and pressure. The relative vapour density is consequently found by dividing the mass of the vapour by the mass of the air displaced.

In order to prevent fracture of the bulb when the small flask which contains the liquid is dropped in, some asbestos is placed at the bottom of the bulb

193. Dumas's Method.—This method[1] is specially adapted for the study of the vapour densities of substances which possess a high boiling point, and for which an apparatus involving the use of mercury fails.

[1] Dumas, *Ann. de Chimie et de Physique*, 2e, tom. xxxiii. p. 337, 1826.

About 15 or 20 grammes of the substance are placed in a thin glass flask B (Fig. 93) of about half a litre capacity, and furnished with a narrow stem p drawn out to a point. A glass flask may be used for temperatures up to about 400° C., the point at which glass begins to soften. For higher temperatures a porcelain vessel may be employed.

The flask is placed in a bath of oil, or some fusible metal, the temperature of which is well above the boiling point of the substance under examination. Wood's fusible alloy is a very suitable substance for such a bath, as it fuses at 70° C., has a high boiling point, and gives off no fumes.

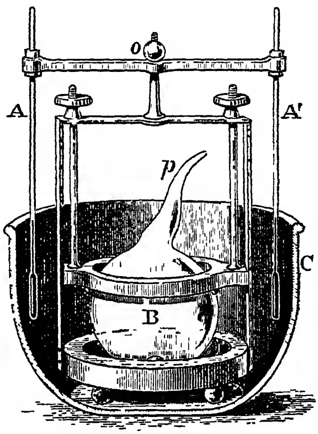


Fig. 93.

When boiling sets in, the air is gradually expelled from the flask, and after some time nothing remains inside but the boiling liquid and its vapour. The temperature of the bath being well above that of the boiling liquid, a strong jet of vapour issues from the nozzle of the flask as long as any liquid is left within. When the liquid is completely vaporised the escape of vapour suddenly ceases and the flask is left filled with vapour, which soon takes up the temperature of the bath. The nozzle is then hermetically sealed, and the flask is removed from the bath, allowed to cool, and its weight determined.

This weight W is the sum of the weights of the glass flask and its contained vapour minus the weight of the air displaced by the flask. Denote these by w_g, w, and w_a respectively, then

$$W = w + w_g - w_a.$$

Before the experiment the flask was weighed open, and its weight W′ represented the difference between the weights of the flask and of the air displaced by the glass constituting it. Denoting these by w_g and w_a' we have

$$W' = w_g - w_a'.$$

Therefore

$$W - W' = w - (w_a - w_a').$$

The last term on the right-hand side of this equation is the weight of the quantity of air which will fill the flask at the temperature and pressure of the atmosphere when the weighing was conducted.

Hence if v_0 is the internal capacity of the flask at zero, $\theta°$ C. and H the temperature and pressure of the air at the time of weighing, we have

$$w_a - w_a' = 0{\cdot}001293 \frac{v_0(1+g\theta)}{1+a\theta} \cdot \frac{H}{760},$$

where g and a are the coefficients of expansion of glass and air respectively. Hence the weight of the vapour is

$$w = W - W' + 0{\cdot}001293 \frac{v_0(1+g\theta)}{1+a\theta} \cdot \frac{H}{760}.$$

Now this weight of vapour filled the flask at the temperature of the bath and the pressure of the atmosphere at the time of sealing the flask. The volume, pressure, and temperature of a known weight of the vapour are therefore known, and its density is determined by the ordinary formula.

On account of the great length of time required to complete an experiment by this method the weights W and W′ are determined at times when the pressure and humidity of the air may differ considerably, and correction in this respect may be necessary. Further, in applying this method great care should be taken to procure the substance under investigation as pure as possible. If any impurity of a higher boiling point than the substance be present, then the substance whose vapour density is sought will vaporise first and the impurity will remain behind to the last, so that the vapour density determined will be that of the impurity or of an exaggerated mixture of the impurity and the substance.

If during ebullition the flask is connected with a partially exhausted chamber, the temperature of ebullition will be greatly reduced, and a modification similar to that applied by Hofmann to Gay-Lussac's apparatus will be introduced. This method of operation has been used by Habermann.

MM. Henri Sainte-Claire Deville and L. Troost,[1] by using a porcelain flask, the nozzle of which could be sealed by an oxyhydrogen blowpipe, have determined the vapour densities of some substances having very high boiling points. Stationary temperature baths were obtained by employing the vapour of such substances as mercury, which boils at 350° C., sulphur 440°, cadmium 860°, and zinc 1040°. The flask was placed inside the vessel in which the vapour was generated, and was protected from radiation to the walls of it by being surrounded by a diaphragm of wire gauze.

[1] Deville and Troost, *Comptes Rendus*, tom. xlv. p. 821; and *Ann. de Chimie et de Physique*, 3e, tom. lviii. p. 257, 1860.

194. Density of Saturated Vapour—Experiments of Fairbairn and Tate.—In order to determine the density of a vapour at the point of saturation with accuracy, it is not legitimate to find the density of the superheated vapour and then deduce that of the saturated vapour, on the assumption that Boyle's law is obeyed up to the point of condensation. The great difficulty to be overcome in the direct determination of the density of a saturated vapour lies in the accurate observation of the volume of a given weight of the vapour when saturated, or exactly at the condensing point.

The principle of the method employed by Fairbairn and Tate[1] for this purpose is illustrated by Fig. 94. Let A and B be two equal globes connected, as shown in figure, by a tube containing mercury, and let A and B contain different quantities of a liquid. For example, let A contain 20 grammes and B 30 grammes, and let the apparatus be placed in a bath the temperature of which can be gradually raised. As the temperature

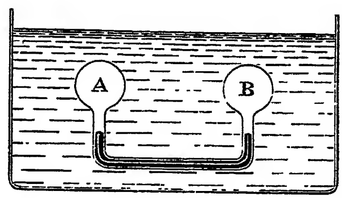


Fig. 94.

rises, more and more of the liquid in each bulb gradually passes into the state of vapour; but as long as any liquid remains in each the pressure will be the same in both, namely, the saturated vapour pressure for the temperature of the bath. A point will, however, be reached at which all the liquid in A will be vaporised and some liquid will still remain in B. Up to this point the level of the mercury in the arms of the connecting tube remains fixed. A small difference of level, arising from the difference of weight of liquid in the two arms, exists, and remains constant till all the liquid is vaporised in one of them. Beyond this point the vapour in A will become superheated and obey the gaseous laws approximately, but the vapour in B will be saturated as long as any liquid still remains. The pressure in B will now increase much more rapidly than that in A, so that the mercury will rise in the arm A. This takes place because the pressure of a saturated vapour increases more rapidly with temperature than that of a superheated vapour.

Hence, if the temperature be noted at which the mercury just begins to rise in A, then it is known that at this temperature the liquid in A is all vaporised and just beginning to be superheated. The volume of the bulb being known and the temperature noted, the pressure may be found from a table of saturated vapour pressures, or it may

[1] Fairbairn and Tate, *Phil. Trans.*, 1860, p. 185; and *Phil. Mag.*, vol. xxi. 1861, p. 230.

be found directly by any form of a pressure gauge, so that the data for finding the density of the vapour at the saturation point are complete.

The experiments were conducted by means of the apparatus shown in Fig. 95. A known weight of water was placed in a glass globe A, which was about 14 cm. in diameter, this globe was furnished with a stem about 80 cm. long and 1 cm. wide, the end of this stem dipped under the surface of some mercury contained in a glass tube which surrounded the stem of A, and was firmly jointed to a metal reservoir B enclosing A. This reservoir and the tube contained some water, so that the interior of B was saturated with water vapour at all the temperatures used in the experiments. The pressure of this vapour was roughly measured by a pressure gauge G, and the temperature was registered by means of a thermometer exposed naked to the vapour, and corrected for the effect of pressure. The temperature being known, the exact pressure can be found from Regnault's tables of vapour pressures. A nozzle p allows of the steam being let off at pleasure.

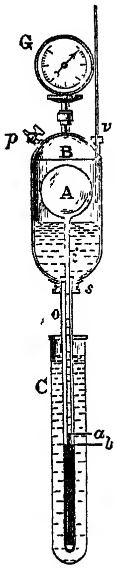


Fig. 95.

The apparatus was heated by placing the end of the tube C in a sand bath, and B was at the same time heated by a gas burner. All the air was expelled from B by boiling for some time with the nozzle p open, and in order to ensure that A should contain no air it was filled with mercury, and inverted with the stem under mercury before the liquid was introduced. As long as any liquid remains in A the vapour pressure will be the same in B and A, and the level of the mercury in the stem of A will remain fixed, but as soon as all the liquid in A is vaporised the mercury will rise in the stem. Before this point the mercury stands somewhat higher inside the stem than outside, on account of the weight of the column of liquid in the tube *ob*. The volume of A being known up to any point in the stem, and the pressure and temperature at which the mercury just begins to rise in the stem being determined, the data necessary for the estimation of the density of the saturated vapour are at hand. In order to determine the saturation point most accurately the vapour in A was superheated 10° or 20° above the point of saturation, and the difference of level *ab* of the mercurial columns was noted with a cathetometer. The temperature was then gradually reduced, and the determination of the saturation point was taken from the observations on the mercurial column when falling in the stem of A rather than when rising.

The results of these experiments show that the density of saturated vapour is invariably greater than that deduced from the laws of gases.

If v denotes the specific volume of the saturated vapour—that is, the volume per unit mass—then, according to the authors of these experiments, the relation between p and v may be written in the form

$$v=a+\frac{b}{p+c}.$$

The values of the constants deduced from the experiments were, if p is measured in millimetres in mercury

$$v=25{\cdot}62+\frac{1257605}{p+18{\cdot}29}.$$

The following table after M. Jamin shows the observed and calculated densities (by the above formula) of saturated water vapour between 58° and 145° C. :—

Temperature in Degrees Centigrade.	Volume in c.c of a Gramme of Water Vapour.		
	Observed	Calculated.	By Boyle's Law.
58·20°	8266	8183	8380
68·50	5326	5326	...
70·75	4914	4900	...
77·20	3717	3766	...
77·50	3710	3740	.
79·40	3433	3478	. .
83·50	3046	2985	.
86·85	2620	2620	...
92·65	2146	2124	2180
117·17	941	937	991
118·23	906	906	...
118·46	891	900	.
124·17	758	758	
128·41	648	669	..
130·67	634	628	
131·78	604	608	..
134·87	583	562	
137·46	514	519	
139·21	496	496	...
141·81	457	461	...
142·36	448	456	.
144·74	432	428	466

Near the point of saturation the coefficient of expansion was almost 5 times that of air, but it gradually approached that of air with superheating.

195. Recent Experiments.—The determination of the densities of saturated vapours was undertaken quite recently by M. Perot.[1] Two methods of experiment were adopted, both of which depended in principle on the isolation and weighing of a certain volume of the saturated vapour. In the first method a glass globe A, similar to that used in Dumas's method (Art. 193), was placed inside a closed vessel B, connected with an air pump. Dry air was repeatedly admitted to and pumped out of B, so that both B and A were thus carefully dried. Finally, the vessel B was exhausted as closely as possible, the residual pressure being only $\frac{1}{2}$ mm. In this process the flask A became exhausted also. The liquid under investigation had been previously sealed up in a glass bulb and placed in B. The temperature was now raised till the bulb burst, and the vessel B, together with the flask A, became filled with saturated vapour. The temperature was now maintained constant for some time, and the nozzle of the flask A was then sealed up electrically. This being done, A was taken out and weighed. This gives the weight of the vapour contained, and hence its density may be found.

In the second method two chambers A and B were connected by a tube furnished with a stopcock. The vapour was generated in one, A, and when the tap was opened the other chamber, B, became filled with saturated vapour. The tap was then closed, and the vapour drawn off from B by means of an aspirator into drying tubes and weighed. The weight of the saturated vapour which filled the chamber B was thus determined, and its density calculated in the ordinary way.

M. Perot found that the two methods gave very concordant results. Thus the specific volume of ether vapour at 30° C. by the first method was 400 c.c., while by the second the specific volume at 30°·02 C. was 399·9 c.c.

In the case of water, temperatures much above 100° C. could not be employed on account of the solvent action of water vapour on glass at high temperatures. The results for water and ether are given in the following tables :—

Specific Volume of Water Vapour in Cubic Centimetres.

Temperature . .	68·2	88·6	98·1	99·6	101·5	124·1
Sp. Vol. . . .	5747	2531	1782	1657	1583	766

[1] Perot, *Journal de Physique*, 2e, tom. vii. p. 129, 1888.

Ether Vapour.							
Temperature .	28·4	30·0	31·7	31·9	57·9	85·5	110·5
Sp. Vol. . .	426·2	400	375·1	373	168	77·77	43·94

In the case of ether the results of the experiments were represented by the formula

$$v = 400{\cdot}42 - 15{\cdot}7394\theta + 0{\cdot}539\theta^2.$$

SECTION V

MIXTURES OF GASES AND VAPOURS

196. Evaporation and Vapour Pressure in a closed Space occupied by a Gas—Dalton's Experiment.—The first trustworthy experiments on the formation of vapours in spaces already occupied by air or other gases were executed by Dalton with an apparatus similar to that depicted in Fig. 96. An air-tight glass flask was fitted with a barometer AM and a delivery tube C, which communicated with an air pump by means of which the flask could be exhausted or the pressure of the gas within it modified at pleasure. A funnel B, furnished with a tap, contained a quantity of the liquid under experiment, and by opening the tap a small quantity of the liquid could be passed into the flask in order that its vapour might be studied. If the flask is exhausted, the first drops of liquid are vaporised immediately after admission; but if the interior is occupied by air or any other gas the evaporation takes place much more slowly, and the greater the pressure of the gas the more slowly does the evaporation take place. In a vacuum the evaporation is rapid, and the vapour quickly attains its maximum pressure; but when air or any other gas is present, the vapour pressure gradually increases, and its progress may be observed by means of the barometer AM with which the flask is furnished. As the evaporation progresses the barometer rises, showing that the pressure within the flask is increasing; and as the volume of the flask and the quantity of gas within it remain fixed, this increase of pressure must be due solely to the formation of the vapour,

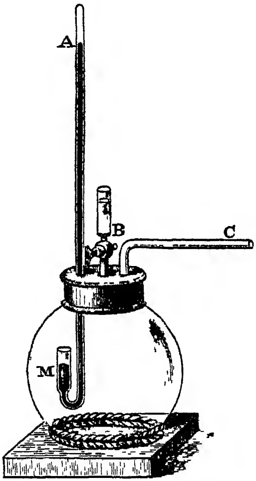


Fig 96.

and may be regarded as the vapour pressure. The total pressure within the flask, from this point of view, is regarded as the sum of the initial pressure of the gas and that of the vapour, and Dalton found that the increase of pressure ultimately produced by the evaporation of a liquid in such a closed space is the same whether the space be filled with a gas or empty, and that this increase is equal to the maximum vapour pressure of the liquid for the temperature at which the experiment is made. In other words, if a space of fixed volume be initially filled with a gas at pressure p, and if a quantity of liquid, whose maximum vapour pressure at the temperature of the experiment is F, be introduced into the space and allowed to evaporate so as to saturate the space, then the final pressure within the space will be

$$P = p + F.$$

The results arrived at by Dalton were subsequently confirmed by Gay-Lussac with the convenient form of apparatus shown in Fig. 97. One of the arms AB of an open air manometer is furnished with a stopcock F, over which a funnel, also furnished with a tap G, can be screwed on. The pin of the tap G is not pierced through with an aperture so as to permit of a continuous flow of liquid from the funnel above, but is merely furnished with a cavity O which when turned upwards becomes filled with the liquid contained in the funnel, and when turned downwards discharges itself into the arm AB below. Thus each time this tap is turned the full of the cavity of liquid is introduced into the space below, and by this means a known quantity of liquid may be placed in the arm AB at any time.

Gay-Lussac.

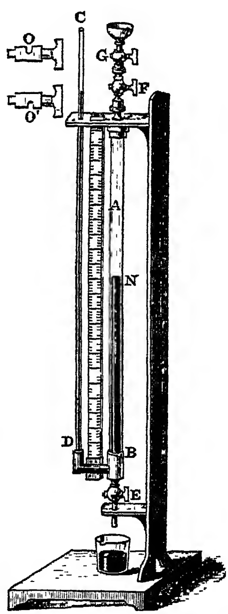


Fig. 97.

In making an experiment the apparatus is first thoroughly dried by means of a current of dry air, and it is then filled with mercury. Some dry gas is then admitted into the arm AB by placing the tap F in connection with a reservoir of the gas, and permitting the mercury to escape through the tap E. These taps are finally closed, and the pressure and volume of the gas in the arm AB noted. Drops of liquid are then introduced by the tap G, and as they evaporate the mercury rises in the arm CD and falls in AB, until the space A becomes saturated. The vapour

has now reached its maximum pressure, and no increase of pressure is produced by the further introduction of liquid.

In this form of the experiment the conditions are not exactly the same as in the experiment of Dalton, for here the space occupied by the gas and vapour increases as the pressure rises, while in Dalton's experiment the space remained constant. Hence, if p and v be the initial pressure and volume of the gas, its pressure p', after the formation of the vapour in the experiment of Gay-Lussac, when the volume has increased to v', will be $p'=pv/v'$, and the final pressure will not be $p+\mathrm{F}$ as before, but will be

$$\mathrm{P}=p'+\mathrm{F}=\frac{pv}{v'}+\mathrm{F}.$$

By observing the pressures P and p and the volumes v and v' the vapour pressure F can be found. The results of the experiments of Gay-Lussac confirmed the conclusion of Dalton that the vapour exerted the same pressure whether in a vacuum or in presence of a gas or mixture of gases, the total pressure of a gaseous mixture being the sum of the pressures which the constituents would exert in the space if they occupied it separately. It was therefore concluded that, at least as far as the resultant pressure is concerned, the mixed gases are without influence on each other.

These experiments were not sufficiently numerous or accurate to establish the general truth of Dalton's law on a sure basis. *A priori* the law does not appear probable, for if several liquids be admitted simultaneously into the flask in the experiment of Dalton, each should produce its maximum vapour pressure independently of the others, and by increasing the number of liquids the total pressure within the flask could be increased indefinitely. The law can therefore be only

Regnault. approximately true within certain limits, and M. Regnault[1] was consequently induced to investigate the behaviour of mixed gases and vapours more closely and completely. The apparatus employed was the same as that used in the determination of the pressure of saturated vapours. Having determined the maximum vapour pressure in a vacuum between zero and 40° C., he repeated the same measurements when the apparatus contained air or nitrogen, and constructed a table of the maximum vapour pressures in presence of these gases:—

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. xv. p. 129, 1845.

Temperature.	Vapour Pressure.		Difference.
	In Air.	In a Vacuum.	
°	mm.	mm.	mm.
0	4·47	4·60	0·13
15·00	12·38	12·70	0·32
21·07	18·28	18·58	0·30
24·69	22·73	23·14	0·40
31·00	32 97	33·41	0·44
35·97	43·39	44·13	0·74
38·00	48·70	49·30	0·60
	In Nitrogen		
0	4·31	4 60	0·29
16·49	13·29	13 96	0·67
21·46	18·61	19·03	0·42
25·50	23·71	24·27	0·56
32·50	35·92	36·38	0·46
37·74	47·80	48 63	0·83
39·81	53·72	54·36	0·64

This table shows that the vapour pressures in the gas are very nearly equal to, but a little less than, the corresponding maximum pressure in a vacuum; and as the measurements in both sets of experiments were made with the same apparatus, this difference cannot be attributed to the apparatus. Regnault feared that the oxygen of the air attacked the mercury, and for this reason he also employed nitrogen, but found the same difference, so that he was forced to the conclusion that the vapour pressure is a little less in a gas than in vacuo. Regnault thought this did not militate against the possible truth of Dalton's law, but considered that it might be explained by the condensation on the walls of the vapour chamber, and perhaps to some extent by the slowness of evaporation in a gas which prevents the final stage being reached. This view appeared to be confirmed by the subsequent work of Herwig.[1] In order to determine the influence of the chamber walls Herwig introduced a small quantity of liquid into the vapour chamber, so that the space was not saturated. He then gradually diminished this space till the vapour became saturated, and further diminution produced condensation. With certain liquids, such as alcohol and bisulphide of carbon, the corresponding pressure was the same as the maximum vapour pressure; but with others, such as ether and water, the pressure continued to increase after the first appearance of dew as the capacity of the vapour chamber was decreased. This effect was more marked as the temperature was lower.

Herwig.

[1] Herwig, *Pogg. Ann.*, Band cxxxvii. p. 592, 1869.

The foregoing experiments show, within the limits to which they were carried, that when a space already occupied by air or any other gas is saturated with a vapour, the pressure exerted by the vapour is practically equal to the maximum pressure which the vapour would exert in vacuo at the same temperature. It was for this reason assumed by Dalton and his followers that the vapour density in the gas—that is, the weight of vapour per unit volume—was the same as in vacuo. This, however, cannot be assumed as a consequence of the fact that the pressures are the same. The point remained to be tested by experiment. The question was finally settled in the affirmative by Regnault.[1] Air saturated with water vapour was drawn by means of an aspirator through a system of drying tubes as in the chemical hygrometer (Art. 204). The volume of air drawn through the tubes was measured by the quantity of water which escaped from the aspirator, and the weight of moisture contained was calculated by weighing the drying tubes before and after the experiment. The following table after Regnault shows how closely the observed and calculated weights agree :—

Vapour density.

Temperature	Weight of Vapour		Difference.
	Calculated.	Observed.	
0	0·273	0·273	0·000
5·85	0·424	0·424	0·000
12·88	0·660	0·653	0·007
14 65	0·736	0·731	0·005
20·57	1·013	1·010	0·003
25·11	1·328	1·315	0·013

We conclude, therefore, that at least within certain limits in a space already occupied by a gas a liquid ultimately evaporates to the same extent as in a vacuum, the process being merely more slow.

197. Dalton's Law.—When several gases which have no chemical action on each other are contained in the same vessel, the pressure of the mixture may be determined by means of a simple rule known as Dalton's[2] law. According to this law the pressure of a gaseous mixture on the walls of the containing vessel is equal to the sum of the pressures which the constituents would exert if each occupied the vessel separately. According to Dalton's view each

[1] *Ann. de Chimie*, 3e, tom. xv. p. 129, 1845.

[2] Dalton, *Memoirs of Manchester Phil. Soc.*, vol. v., 1802, p. 543.

gas in the mixture may be considered as diffused throughout the whole vessel, so that all occupy the same volume, namely, the whole chamber.

If the gases be taken as ideal substances obeying Boyle's law, and if the molecules in the mixture are outside the sphere of each other's attraction—that is, if they move about independently of each other, except in so far as collisions may occur, then the bombardment on the walls of the containing vessel by the molecules of the mixture will be equal to the sum of the actions which would be exerted if each gas occupied the whole space separately. There will, however, obviously be a limit beyond which the law will cease to be true and become more and more inaccurate. If the number or the quantities of the gases in a given space be greatly increased, or, what is the same thing, if the space occupied by a given mixture is largely reduced so that the pressure of the mixture is great, then the molecules will not possess the freedom of motion necessary for the truth of the law. They will, under the great pressure, be brought into such close proximity that the motion of any molecule will be influenced by the others. The free path will be lost to some extent, and the molecular motion will begin to acquire the characteristics of that which occurs in a liquid. Boyle's law will be more and more departed from, and as a consequence Dalton's law will also cease to be true (cf. Arts. 55 and 56).

If, however, the gases are far removed from their condensing points, so that we may assume Boyle's law to hold for each constituent as well as for the mixture as a whole, then the sum of the products pv for the constituents will be equal to the product PV for the mixture, or

$$p_1v_1+p_2v_2+p_3v_3+\ .\ .\ .\ =\mathrm{PV}.$$

If, now, each gas is diffused throughout the whole chamber, as Dalton supposed, then

$$v_1=v_2=v_3=\text{etc.}=\mathrm{V},$$

so that the equation becomes

$$\mathrm{V}(p_1+p_2+p_3+\text{etc.})=\mathrm{PV},$$

or

$$\mathrm{P}=\Sigma p$$

—that is, the whole pressure is the sum of the partial pressures.

If, on the other hand, the gases are superimposed on each other in layers, they will have a common pressure P and

$$\Sigma v=\mathrm{V}.$$

But in this case we have also

$$Pv_1=p_1V,\ Pv_2=p_2V,\ \text{etc.},$$

so that

$$\Sigma p=P\frac{\Sigma v}{V}=P$$

—that is, the total pressure P is equal to the sum Σp of the pressures which the gases would exert if they each occupied the vessel separately.

In the case of vapours the law is approximately obeyed within certain limits and with certain restrictions. In 1815 Gay-Lussac [1] found that the vapours of alcohol and water mix like two gases which have no action on each other, the density and pressure of the mixed vapours agreeing closely with that deduced according to Dalton's law. In 1836 Magnus [2] proved that when two liquids which do not mix are introduced into the vacuum of a barometer tube, the pressure of the mixed vapours at any temperature is equal to the sum of the vapour pressures of the two liquids. But when the liquids possess the property of mixing with each other, the behaviour of the vapour is greatly modified. The pressure of the mixed vapours is no longer equal to the sum of the pressures of its constituents acting separately, but is always less than this sum, and often less than the vapour pressure of the most volatile constituent. This appears to contradict the observations of Gay-Lussac on the pressure of the mixed vapours of alcohol and water; but, as Magnus has pointed out, the conditions under which Gay-Lussac's experiment was made differed from those by which these conclusions were established. In Gay-Lussac's experiment the mixture of water and alcohol was completely vaporised, whereas in those of Magnus an excess of the mixed liquids was always present in contact with the vapour.

Mixtures.

The matter was subsequently investigated by Regnault [3] in his work on the elastic force of vapours, and his experiments confirmed the conclusions of Magnus. Thus it was established that the pressure of the vapour of a mixture of two or more liquids which do not mutually dissolve each other was equal to the sum of the vapour pressures of the constituents considered separately, at the same temperature; but volatile liquids which mutually dissolve each other gave a complex vapour pressure which was always less than the sum of the vapour pressures of its constituents. Thus when water is mixed with a substance, such as sulphuric acid, which is said to have a strong

[1] Gay-Lussac, *Ann. de Chimie*, tom. xcv. p. 314, 1815.

[2] Magnus, *Pogg. Ann.*, Band xxxviii. p. 488, 1836.

[3] Regnault, *Mem. de l'Académie*, tom. xxvi. p. 722.

"affinity" for it, the vapour pressure of the mixture diminishes as the proportion of acid is increased. A weak solution has nearly the same vapour pressure as pure water, while the vapour pressure of a very strong solution is almost zero at ordinary temperatures. Regnault also extended his work to mixtures of gases and vapours, and concluded that in these cases Dalton's law is very closely obeyed, and that in all the cases examined it would probably have been verified rigorously but for the action of the walls of the enclosing vessel.

These conclusions cannot, however, be pushed beyond certain limits. As already pointed out, if the pressure be increased, the vapours and gases cease to obey Boyle's law approximately, and Dalton's law ceases to be true under the same conditions. The pressures under which the foregoing experiments were conducted did not exceed two atmospheres, and for this reason Andrews[1] took up the question and examined the properties of a mixture of nitrogen and carbon dioxide under high pressures. The results of his investigation led him to conclude that under high pressures Dalton's law is largely deviated from, and that it is probably only strictly true for gases in the so-called perfect state.

It appears from the experiments of Andrews that when strongly compressed carbon dioxide and nitrogen are mixed, a notable expansion occurs, varying from 9 % at 50 atm. to as much as 39 % at 80 atm., when 3 volumes of nitrogen were mixed with 4 volumes of carbon dioxide. On the other hand, no very marked difference was found between the total pressure and the sum of the partial pressures. A series of investigations with various gases has been made by F. Braun[2] which shows that when two gases, at the same pressure in different vessels connected by stopcocks, are allowed to mix, a change of pressure occurs consequent on the mutual action of the two gases. This change may be either positive or negative. Thus there appears to be a decrease of pressure when SO_2 mixes with CO_2, hydrogen, nitrogen, or air, and an increase of a fraction of a millimetre when hydrogen mixes with CO_2, air, or nitrogen.

HYGROMETRY

198. Fraction of Saturation, or Humidity.—The atmosphere consists of a mixture of oxygen, nitrogen, and aqueous vapour, together with some impurities in small quantity. The percentage of

[1] Andrews, *Phil. Trans.*, 1886-87.

[2] F. Braun, *Wied. Ann.*, Band xxxiv. p. 943, 1887.

vapour is very variable, depending on the temperature and other modifying circumstances. We have already seen that at a given temperature a given space will contain a certain definite weight of vapour at its maximum pressure. This is the greatest weight of vapour which the space can accommodate, and at this point the space is said to be saturated or filled with saturated vapour. It has been proved, moreover, by Regnault (Art. 182) that the presence of a gas, at least at ordinary pressures, does not affect the quantity of vapour which a given space can contain. It merely affects the rate of evaporation; but ultimately the quantity of vapour at the saturation point that can be contained in a given space is the same whether the space is vacuous or contains air or other gases. The quantity of vapour required to saturate a given space depends only on the temperature, and when the temperature is known, the pressure of the saturated vapour can be found from the tables of saturated vapour pressures already compiled by Regnault and others.

If the space is not saturated, however, the vapour pressure will be less than the maximum value for the corresponding temperature. The ratio of the actual pressure of the vapour in a space to the maximum, or saturation pressure for the same temperature, is called *the fraction of saturation.* It is on this element that our opinions of the dryness or dampness of the atmosphere are chiefly formed. The air is ordinarily said to be damp when it is saturated or nearly saturated with vapour. It is not the absolute quantity of vapour in the air that determines its dampness, but merely the proximity to saturation. For example, an atmosphere saturated at 10° C. will be not nearly saturated at 20° C., although the quantity of vapour in it is exactly the same at the latter temperature as at the former. Heating an atmosphere lessens the fraction of saturation, and cooling increases it if the quantity of vapour in the atmosphere be kept constant. The fraction of saturation is often referred to as the *humidity*, or relative humidity of the air, since our sensations of dryness and dampness depend rather upon this factor than upon the absolute quantity of vapour present. Thus in winter the humidity of the air is generally much greater than in summer, although the quantity of vapour present in the winter may be much less, on account of the lower temperature, than in summer.

The fraction of saturation may also be expressed as the ratio of the weight w of vapour contained in a given space to the weight W of the quantity which would saturate the same space at the same temperature. For if the vapour obeys Boyle's law up to the point of saturation (which is approximately the case), then the weight contained

in a given volume is simply proportional to the pressure, and we have the equation

$$\frac{w}{W}=\frac{f}{F}.$$

It thus appears that two general methods are available for determining the fraction of saturation, or humidity, of the atmosphere. One by ascertaining directly the weight w of vapour in a measured volume of air, and then ascertaining from Regnault's tables the weight W of vapour which would saturate the same volume at the same temperature. This is the method practised in the chemical hygrometer. The other method consists in determining the actual pressure f of the vapour in the air, and then ascertaining the maximum pressure F at the same temperature, from the tables of vapour pressures. This is the method practised in all dew-point instruments.

199. The Dew-Point.—If an atmosphere containing some aqueous vapour be gradually cooled, a temperature will be reached at which the vapour will begin to condense. This temperature is called the dew-point. It is obviously the temperature at which the quantity of vapour actually present would saturate the air, and it depends therefore only on the absolute quantity of vapour present per unit volume.

When the dew-point is known, the pressure f of the vapour in the air can be found at once. For suppose we have a body A, the temperature of which can be gradually reduced. As the temperature of A falls a point will be reached at which dew will begin to be deposited on its surface. Hence at this temperature the vapour around the body A is at its maximum pressure, for at this temperature and under this pressure (namely f, the vapour pressure sought) condensation is taking place. The actual pressure of the vapour in the air is therefore equal to that which would bring it just to the condensing point at the temperature of the dew-point. In other words, the actual pressure of the vapour is equal to its maximum pressure at the temperature of the dew-point. If, therefore, the dew-point is known, the maximum pressure for this temperature can be found in the tables of vapour pressures, and this is the actual pressure f of the vapour in the air. The fraction of saturation then will be the ratio of the maximum vapour pressure f at the dew-point to the maximum pressure F at the temperature of the air.

200. Dew-Point Hygrometers.—All dew-point hygrometers are merely instruments for determining the dew-point, and depend in construction on some method of cooling a body gradually in the air till dew begins to be deposited on it. In the construction of such an instrument the two objects to be kept in view are: (1) an accurate means

of determining the instant at which dew begins to be deposited, and (2) an exact knowledge of the temperature of the surface when the deposition of dew just begins.

A phenomenon commonly observed in dining-rooms is the deposition of moisture on the surface of a glass containing cold water. When water-carafes are filled with cold water and placed on the table of a warm dining-room, it often happens that their surfaces become covered with a deposit of dew which sometimes accumulates to such an extent that drops of liquid trickle down the sides of the vessel. This happens because the temperature of the water is lower than the dew-point of the air in the room, and, as a consequence, the vapour condenses on the surface of the carafes or water-glasses, and continues to do so till the temperature of the water rises to the dew-point. If the temperature of the water were noted when it is just cold enough to produce condensation, we would then have the dew-point, and thence the fraction of saturation.

A similar condensation occurs on the surface of a tumbler containing water in which some ice is placed. If the ice,[1] or ice-cold water were carefully added, the temperature could be gradually reduced to the dew-point and an observation made. The temperature of the water when the dew is first observed will be somewhat below the correct dew-point, for when the dew is observed, it means that the condensation has started some time previously. A correction may, however, be applied by taking a second reading of the temperature when the water is allowed to stand till the dew disappears from the surface of the glass. During this period the temperature of the water rises by radiation from the warm chamber, and as soon as it exceeds the dew-point, evaporation occurs at the surface of the glass and continues till all the previously deposited dew disappears. The temperature of the surface at which this occurs is somewhat above the dew-point.[2] The mean of the two is therefore taken as the dew-point.

A glass vessel is, however, not good for making such an experiment, because glass is not a good conductor of heat. For this reason, when the temperature of the water is falling, the outside surface of the glass will always be warmer than the water, and when the water is rising in temperature, the outside surface of the glass will be again warmer than the water if we suppose the heat to pass through the glass to the water, as always occurs in the dew-point instruments employed.

[1] This was the method first suggested by Le Roi in 1771; see also Daniell's *Meteorological Essays and Observations*, London, 1823.

[2] The temperature of the water within the glass may, however, be still below the dew-point.

The thicker the glass and the more badly it conducts, the greater will be the errors thus introduced. For this reason a thin metallic vessel will be much better suited for the purposes of the experiment. Silver is one of the very best conductors of heat, and its surface takes a beautiful polish, on which the slightest deposition of dew can be easily noticed, especially if a similar silver vessel, on which no dew is deposited, be placed beside it for the sake of comparison. This, in fact, is the principle of Regnault's dew-point hygrometer, which will be described immediately. Indeed, a single thin polished cup, the mouth of which is covered or closed by a cork, could be used for determining the dew-point with rapidity, and probably with greater accuracy than some of the more elaborate apparatus invented for the purpose. Ice-cold water could be siphoned as slowly as desired into the cup from another closed vessel, so that the air would not be affected by evaporation from any exposed liquid, and the temperature of the cup could be thus varied by small amounts at the dew-point, and its position could be repeatedly fixed.

201. Daniell's Hygrometer.—One of the oldest and most objectionable forms of direct dew-point hygrometers is that invented by Daniell.[1] This instrument (Fig. 98) consists of a bent glass tube furnished with a pendent bulb at each end. One of these A is naked and made of black glass. This bulb contains some ether, in which the bulb of a very sensitive thermometer dips. All air is expelled from the apparatus by boiling the ether previous to closing, so that it contains only the volatile liquid ether and its vapour. The other bulb B is made of ordinary glass and covered with a muslin or linen rag.

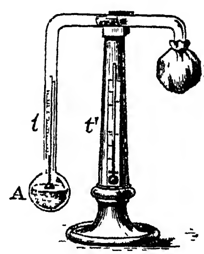


Fig. 98

In making an experiment the ether is all passed into the naked bulb, and the rag covering the other is moistened with ether. The evaporation of this cools the covered bulb and causes condensation of the vapour within. This gives rise to evaporation of the liquid in the naked bulb and consequent cooling. The temperature of the naked bulb thus gradually falls, and by carefully watching its surface, the temperature at which dew first appears can be noted. This temperature is given by the thermometer within the bulb. The apparatus is now allowed to stand till evaporation ceases, and its temperature begins to rise again. The deposit of dew soon disappears, and the temperature at which this occurs is also noted. The mean of these two temperatures is usually taken as that of the dew-point.

[1] Daniell, *Meteorological Essays and Observations*, London, 1827.

The temperature of the surrounding air is given by a thermometer attached to the stem of the instrument. The naked bulb is made of black glass in order to facilitate the observation of the deposition of dew, but, as already remarked, glass is a bad conductor, and consequently the temperature indicated by the thermometer within the bulb may differ considerably from that of the external surface of the bulb at the instant the dew appears or disappears. In both cases the temperature of the external surface is what is wanted, and in both cases this will be higher than that of the liquid within, for the liquid within is colder than the atmosphere, and throughout the whole experiment the flow of heat is from without inwards.

In this instrument the evaporation takes place at the surface of the liquid, and as the liquid mass is at rest, the surface layer will always be colder than the lower parts. Dew will consequently be deposited first at the level of this layer, and if the bulb of the thermometer be plunged below the surface, the temperature indicated by it will be too high. The presence of the observer close to the apparatus is objectionable, and in addition the rate of evaporation cannot be sufficiently controlled. The pollution of the air by the evaporation of ether from the covered bulb is also objectionable.

202. Dines's Hygrometer.—A more recent and less objectionable form of dew-point instrument is that invented by Dines (Fig. 99).

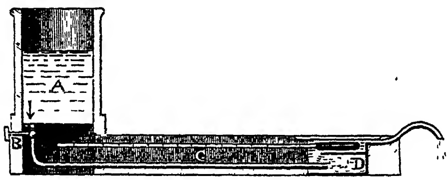


Fig. 99.

This consists of a vessel A, fitted with a pipe through which cold water can flow into a double chamber D. This chamber contains the bulb of a delicate thermometer, and is closed above by a plate of black glass (or silver, which, for the reasons already mentioned, is better). Previous to the experiment, the chamber D is full of water at the temperature of the air, and some cold water or ice and water is placed in A. The tap B is then opened so as to allow the cold water to flow slowly into D. The temperature of this chamber is thus gradually reduced, and when sufficiently cooled, a deposit of dew appears on the surface of the glass plate. The thermometer is then read, and the flow of water stopped. The dew soon disappears and the temperature is again noted, the mean of the two temperatures being taken as before

to represent the dew-point. The operation may be repeated again as often as desired, while any water remains in A at a temperature lower than the dew-point. The observation of the deposition of dew on the glass plate may be facilitated by viewing it by means of a beam of light reflected from its surface. As soon as any dew is deposited the surface becomes dulled, and the intensity of the reflected beam is greatly reduced. An adjacent plate on which dew is not deposited would facilitate the determination of the instant at which dew is deposited on the other plate by comparison, as in the case of Regnault's hygrometer, which we shall now describe.

203. Regnault's Hygrometer.—The most perfect form of dew-point instrument is that devised by Regnault,[1] and employed in his studies in hygrometry. The essential part of the apparatus is a glass tube D (Fig. 100) open at both ends, to the lower end of which a thin polished silver thimble is attached. This thimble contains ether or some other volatile liquid, such as alcohol. The upper end of the tube is closed air-tight by a cork, through which pass the stem of a thermometer T and an open piece of bent glass tubing A the lower end of which penetrates nearly to the bottom of the liquid contained in the thimble. A tubulure in the side of this tube fits into a vertical brass tube which forms the support of the apparatus. The lower end of this brass tube is connected with an aspirator, by means of which a current of air can be drawn through the system, entering by the bent glass tube A and bubbling

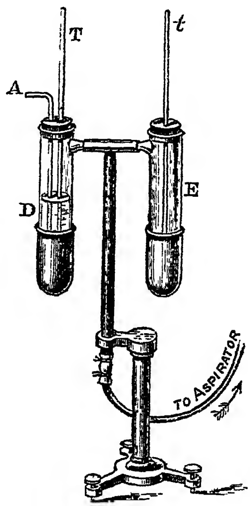


Fig. 100.

through the ether. By this means evaporation of the liquid is produced with consequent cooling, and dew is deposited on the surface of the polished silver. In order to facilitate the observation of this, a second tube E with a similar thimble is supported beside that just described. This tube is empty, and merely carries a thermometer t which gives the temperature of the air. Thus by comparison of the two silver thimbles the moment at which the dew appears or disappears can be ascertained with great delicacy. The aspirator is placed at a convenient distance, and the apparatus is viewed through a telescope, also situated at a distance. The air around the apparatus is thus undisturbed by the breath and

[1] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. xv. p. 129, 1845.

presence of the observer, and the flow of liquid through the aspirator can be so nicely controlled that the temperature at which the dew appears will be almost exactly the same as that at which it disappears. If the aspirator is controlled with great delicacy, the dew may be even made to appear and disappear without any observable change in the reading of the thermometer. The process of cooling by the bubbling of air through the ether is a great advantage, for by this means the liquid is kept well stirred and at a uniform temperature throughout. This is the temperature registered by the

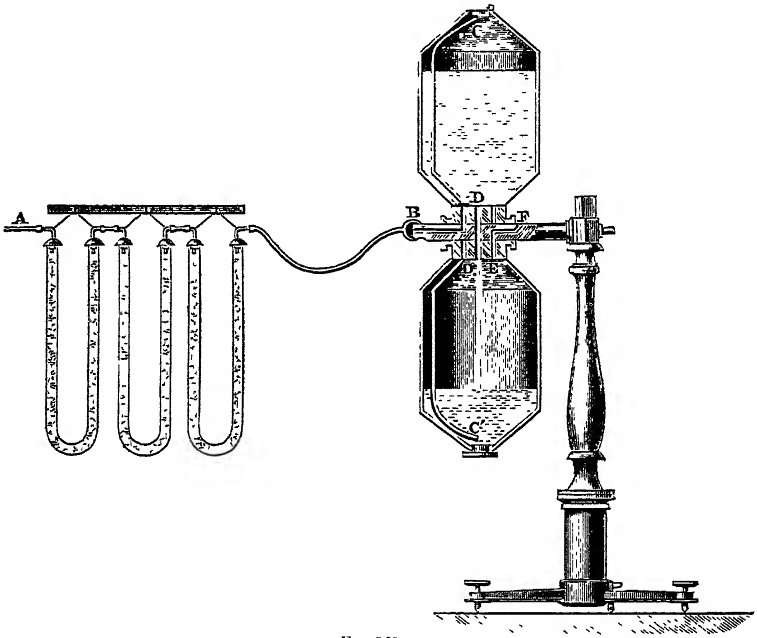


Fig. 101

thermometer, and it cannot differ very sensibly from that of the surface on which the dew is deposited, since the thimble is thin and a good conductor. The other obvious advantages of the method are the absence of the observer from the neighbourhood of the apparatus, and the delicacy with which the flow from the aspirator can be controlled.

204. The Chemical Hygrometer.—The fraction of saturation may be obtained by the direct determination of the weight of vapour contained in a measured volume of the air. This method seems to have been first employed by Brunner,[1] and it leaves nothing to be

[1] Brunner, *Ann. de Chimie et de Physique*, 3e, tom. iii. p. 305. 1841.

desired in point of accuracy. The air is drawn by means of an aspirator CDC′ (Fig. 101) through a series of drying tubes filled with fragments of pumice-stone soaked in sulphuric acid, where all the moisture is deposited and the dry air alone arrives in the aspirator. The last tube, viz. that next the aspirator, is intended to absorb any vapour which may come from the aspirator. The remaining tubes are weighed before and after the experiment, the difference of weight giving the weight of vapour deposited. This is the weight of vapour contained in a volume V of air as registered by the aspirator. This is not the volume which the same mass occupied in the atmosphere before being drawn through the tubes. In the aspirator it is saturated with vapour at its maximum pressure F, corresponding to the temperature θ of the aspirator. This is given by a thermometer inserted. In the air this mass contained vapour at some unknown pressure f and temperature θ'. The problem then is to find the volume V′ at pressure $\mathrm{H}-f$ and temperature θ' of a mass of air whose volume is V at pressure H − F and temperature θ. This, by the formula $vp = \mathrm{R}(1 + \alpha\theta)$, is

$$\mathrm{V}' = \mathrm{V}\frac{\mathrm{H}-\mathrm{F}}{\mathrm{H}-f}\,\frac{1+\alpha\theta'}{1+\alpha\theta}.$$

This, then, is the volume of the vapour drawn in, and its weight is w. Consequently we have

$$w = \mathrm{V}'\rho = 0\cdot001293 \times 0\cdot622\frac{\mathrm{V}'}{1+\alpha\theta'}\cdot\frac{f}{760}.$$

The equation for f, the actual pressure of the vapour in the air, is

$$w = 0\cdot0008 \times \frac{\mathrm{H}-\mathrm{F}}{\mathrm{H}-f}\,\frac{f}{760}\cdot\frac{\mathrm{V}}{1+\alpha\theta}$$

or

$$f = \frac{760w\mathrm{H}(1+\alpha\theta)}{760w(1+\alpha\theta)+0\cdot0008\mathrm{V}(\mathrm{H}-\mathrm{F})}.$$

This method, although possessing the advantage of depending ultimately on a weighing, which is the most accurate process in physical investigation, is, nevertheless, exceedingly tedious in practice. It is not suited besides to indicate rapid changes in the hygrometric state of the air, but rather measures the mean value of the humidity during the time of the experiment. In this respect it is analogous to a voltameter which measures the mean value of an electric current during a certain period. Whereas, a dew-point instrument, especially Regnault's, by its rapidity of action will indicate fairly well the continuous changes of humidity. These instruments then possess in a greater degree the property of being continuous registers of

humidity as galvanometers are continuous registers of the strength of electric currents. The continuity is not, however, complete; but we shall now consider a class of instruments which are continuous in their action.

205. Hygroscopes, or Empiric Hygrometers.—Any instrument which indicates changes in the humidity of the air is called a hygroscope. Many substances possess the property of absorbing moisture from the air or surrounding bodies, and such substances are

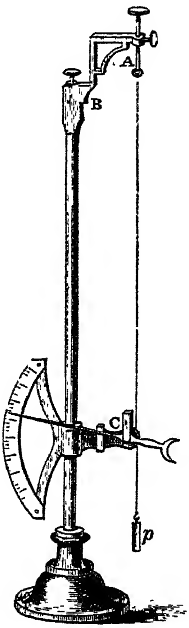


Fig. 102

Fig. 103.

said to be hygroscopic.[1] Most substances consisting of organic tissue are hygroscopic and change their length when they absorb or part

[1] The behaviour of various hygrometric substances has been recently investigated by H. Dufour (*Beiblätter der Physik*, No. VII., 1887; or *Phil. Mag.*, vol. xxiv. p. 296, 1887). Denoting the ratio of the weight of aqueous vapour absorbed to the weight of the dry substance by α, and the coefficient of hygrometric expansion by β—that is, the total expansion which a bar of unit length of the substance undergoes when it has absorbed the maximum amount of aqueous vapour—he finds

Substance.	α.	β.
Horn (10 mm. thick)	0·10	0·061
Gelatine	0·34	0·108
Goldbeater's skin	0·43	0·060

The last substance is that which he most strongly recommends.

with moisture. Such substances besides do not change much with change of temperature; their changes of volume depend chiefly on moisture. Thus it is well known that ropes and catgut strings grow shorter when moistened, and the same is true of twisted strings in general as the twisted fibres swell when wet. It is for this reason that fiddle-strings and tightly-strung tennis-bats often fracture in damp weather. A hair, on the other hand, increases its length when moistened, and this fact was first utilised by de Saussure [1] in the construction of a hygroscope.

A hair is ordinarily covered with a film of oil which protects it from the action of moisture. In order to render it sensitive to changes of humidity, all the surface grease should be removed by boiling for about half an hour in a solution of carbonate of soda, in which it is then allowed to cool. The hair is now ready to act as a hygroscope, and should not be handled or roughly used. One end A (Fig. 102) of it is fixed, and the other extremity, after passing round a small pulley C, is attached to a light spring or a small weight p which keeps the hair stretched. When the hair contracts or elongates the wheel rotates, and a hand attached to it moves over a scale and indicates roughly the relative humidity of the air. The scale may be graduated by direct comparison with a dew-point instrument. De Saussure's instrument has been modified by Monnier, so that the hair passes round four pulleys (Fig. 103) situated on a circular dial, and is kept stretched by being attached to a light spring. The instrument in this form is portable. The indications of hair hygrometers are, however, very variable, and their use has been abandoned in this country for all scientific purposes. The work of Regnault [2] conclusively proved that no rule could be laid down for the graduation of such instruments, for not only do different instruments, graduated and prepared in the same way, differ in their indications, but each instrument is not self-consistent.

206. The Wet and Dry Bulb Hygrometer.—This instrument is that which is almost universally used for continuous records of humidity, and depends in principle on the cooling produced by evaporation. It seems to have been first proposed by Sir John Leslie,[3] who converted his differential thermometer into a hygrometer,

[1] De Saussure (Horace-Bénédict), *Essai sur l'Hygrométrie*, Neuchâtel, 1783.

[2] Regnault, *Ann. de Chimie et de Physique*, 3e, tom. xv. p. 141, 1845.

[3] It was subsequently introduced by Mason, and is often called Mason's hygrometer in this country, and August's psychrometer on the Continent. It was known to Muschenbroek that a thermometer with a wet bulb always indicates a lower temperature than one which is dry, and Hutton, the geologist, is reputed to have used a wet bulb thermometer as a hygrometer.—Leslie (Nicholson's *Journal of Nat. Phil.*, vol. iii. p. 461).

by keeping one of the bulbs moist and the other dry, and noting the difference of temperature.

The instrument as generally used consists of two exactly similar delicate thermometers B and C (Fig. 104), the bulb of one being kept moistened by means of a cotton wick or film of muslin surrounding the bulb and dipping in a small covered vessel of water placed some inches to the side. The other thermometer is placed on the same stand and registers the temperature of the air. Evaporation takes place more or less rapidly from the damp cotton, and the bulb of the thermometer which it covers is cooled more or less according to the humidity of the air. If the air is saturated with vapour no evaporation will take place, and the two thermometers indicate the same temperature.

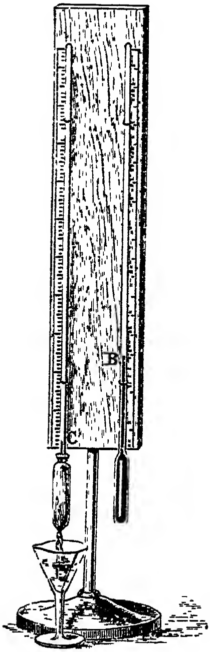


Fig. 104.

The power of the wick to keep up the supply of moisture is much improved by boiling it in a solution of carbonate of soda to remove all grease, but in frosty weather the supply may be completely cut off by the freezing of the water. An objection to the instrument is the difficulty of managing it in frost. In this case, when the wick ceases to act, the bulb must be moistened before making an observation, and some time allowed for freezing and subsequent evaporation from the ice.

In an instrument like this, whose indications depend upon so many complex circumstances, it seems impossible to deduce any theoretic formula connecting the difference of temperature of the two thermometers with the corresponding hygrometric state of the air. The problem has been attacked with partial success by several scientists, and was proposed for consideration by the British Association on the occasion of its first meeting held at York. For this reason tables have been compiled by Glaisher[1] which give the dew-point corresponding to any difference of reading between the thermometers. These tables were constructed by comparing the reading of the wet and dry bulb hygrometer with simultaneous determinations of the dew-point taken by means of a Daniell's hygrometer for a long series of years at Greenwich Observatory, together with a corresponding series taken in

[1] Glaisher, *Hygrometrical Tables*, adapted to the use of the Dry and Wet Bulb Thermometer. London: Taylor and Francis.

India and at Toronto. According to these tables, the difference between the dew-point and the wet bulb reading bears a constant ratio Rule. to the difference of reading of the two thermometers when the temperature of the dry bulb thermometer remains constant. At 53° F. the reading of the wet bulb thermometer is the arithmetic mean between the dew-point and the temperature of the air, or dry bulb thermometer. At higher temperatures the reading of the wet bulb is lower than this mean, and at lower temperatures it is higher.

207. Apjohn's Formula.—A formula connecting the pressure of the vapour in the air with the readings of the wet and dry bulb thermometers has been deduced on certain assumptions by Dr. Apjohn[1] If the temperature of the wet bulb is stationary, the heat necessary to sustain the evaporation must be equal to that supplied by other sources. Let θ_1 be the temperature of the dry bulb, that is the temperature of the atmosphere, and θ_2 that of the wet bulb. Then θ_2 is less than θ_1, so that the wet bulb receives heat by radiation from surrounding objects at a rate proportional to $(\theta_1 - \theta_2)$. Dr. Apjohn assumed that the thin layer of air in contact with the wet bulb at any instant falls from θ_1 to θ_2, and that this cooling furnishes the whole supply of heat. It is next assumed that this layer of air, which approaches the wet bulb at a temperature θ_1, and contains vapour at a pressure f, becomes saturated with vapour at θ_2 and pressure F_2. It is clear, however, that in practice neither of these conditions will be realised. On these assumptions, however, the heat lost in any time is that which will evaporate sufficient water at θ_2 to saturate a volume v of air, that is to increase its vapour tension from f to F_2, while the heat gained is that lost by the same volume of air in falling from θ_1 to θ_2. Let w_0 be the weight of the volume v of air at zero and 760. Then the weight of the same volume at θ_2 and pressure H will be

$$w = \frac{w_0}{1+\alpha\theta_2} \frac{H}{760} = \varpi H \text{ (suppose)},$$

and the weight of an equal volume of vapour at pressure $(F_2 - f)$ and temperature θ_2 will be, as ρ is the relative density of aqueous vapour,

$$w' = \rho \frac{w_0}{1+\alpha\theta_2} \frac{F_2 - f}{760} = \varpi\rho(F_2 - f).$$

Hence the quantity of heat received by the wet bulb will be $ws(\theta_1 - \theta_2)$ and that lost will be Lw', where s is the specific heat of air and L the latent heat of water at θ_2, consequently for equilibrium we have the equation

$$Lw' = ws(\theta_1 - \theta_2),$$

or

$$f = F_2 - (\theta_1 - \theta_2)\frac{sH}{L\rho},$$

where f is the actual pressure of the vapour in the air, and F_2 the maximum vapour pressure at the temperature θ_2 of the wet bulb. Using the values of the quantities s, L, ρ known at this time, Apjohn found the coefficient $\frac{s}{L\rho} = \frac{1}{87 \times 30}$ when the temperature θ_2 is above the freezing point, so that the formula became

$$f = F_2 - \frac{\theta_1 - \theta_2}{87} \cdot \frac{H}{30},$$

[1] Apjohn, *Trans. Roy. Irish Academy*, vol. xvii. p. 275, 1834-35.

in which the temperature is measured in degrees Fahrenheit, and the barometric height H is measured in inches. Below the freezing-point L must be replaced by the sum of the latent heats of liquefaction and vaporisation, and the formula becomes

$$f=F_2-\frac{\theta_1-\theta_2}{96}\frac{H}{30}.$$

It has been assumed above that a volume v of air is cooled from $\theta_1°$ to $\theta_2°$, but in the actual case this volume of air contains vapour at a pressure f, and the cooling of this vapour from $\theta_1°$ to $\theta_2°$ ought also to be taken into account. This factor is taken account of in the formula deduced by Dr. August, but otherwise the assumptions are the same as those of Apjohn. The radiation from surrounding objects is neglected by both, as well as the fact that the air is probably never quite saturated by contact with the wet bulb. For this reason the humidity given by these formulæ is generally too great, especially in dry or calm weather. In calm weather this is probably owing to radiation, which elevates the reading of the wet bulb.

208. August's Formula.—If the supply of heat in any time arises from the cooling of a volume v of air mixed with a volume v of vapour at pressure f, then as before the heat absorbed by evaporation is

$$Lw'=L\varpi\rho(F_2-f),$$

while that supplied will be, for the volume v of air which is at θ_2 and $(H-F_2)$, and weight w_1

$$sw_1(\theta_1-\theta_2)=s\varpi(H-F_2)(\theta_1-\theta_2),$$

and for the same volume of vapour at pressure f, specific heat s', and weight w_2

$$s'w_2(\theta_1-\theta_2)=s'\rho\varpi f(\theta_1-\theta_2).$$

Consequently for equilibrium we have

$$L\rho(F_2-f)=s(H-F_2)(\theta_1-\theta_2)+s'f\rho(\theta_1-\theta_2).$$

Hence

$$f\rho[L+s'(\theta_1-\theta_2)]=F_2[L\rho+s(\theta_1-\theta_2)]-sH(\theta_1-\theta_2),$$

from which we have

$$f=F_2\frac{1+\frac{s}{\rho L}(\theta_1-\theta_2)}{1+\frac{s'}{L}(\theta_1-\theta_2)}-H\frac{\frac{s}{\rho L}(\theta_1-\theta_2)}{1+\frac{s'}{L}(\theta_1-\theta_2)},$$

and observing that L is large compared with s or s', this may be written in the approximate form

$$f=F_2-\frac{sH}{\rho L}(\theta_1-\theta_2),$$

which is the same as that deduced by Apjohn. If we take $s=0{\cdot}237$, $\rho=0{\cdot}622$, and $L=600$, we find

$$f=F_2-0{\cdot}000635(\theta_1-\theta_2)H,$$

when f and f_2 are measured in the same units as H, namely millimetres, and θ_1 and θ_2 in degrees centigrade.

The action of this hygrometer was carefully investigated by Regnault,[1] who

[1] Regnault, *Mémoire sur l'Hygrométrie*, *Ann. de Chimie et de Physique*, 3e, tom. xv. p. 201, 1845.

found that its indications were seriously affected both by radiation and by the velocity of the wind. Thus if the two thermometers are placed in a tube in a current of dry air, we have $f=0$, since the air is dry; consequently, by the formula, $\theta_1-\theta_2$ should be proportional to F_2, but θ_1 is constant, and if θ_2 falls, $\theta_1-\theta_2$ increases, therefore F_2 should increase, which is impossible, since F_2 decreases with θ_2. The only solution then is that θ_2 should remain constant, and this was found not to be the case, but $\theta_1-\theta_2$ increased largely with the velocity of the current.

SECTION VI

ON THE CONTINUITY OF STATE

209. Critical Temperature — Experiment of Cagniard de La Tour.—When the temperature of a liquid contained in an open vessel reaches a certain point, depending on the pressure and the nature of the liquid, boiling sets in. This ceases to be the case, however, when a liquid is heated in a closed vessel. Here, at any given temperature, the space above the liquid becomes filled with saturated vapour, the pressure and absolute density of which depend on the temperature. As the temperature rises, the average kinetic energy of the molecules of the liquid increases, and they are projected in increasing numbers into the space above, so that the pressure of the vapour increases with the temperature; the pressure supported by the liquid at any temperature is that of the saturated vapour at that temperature, and, as a consequence, the formation of bubbles in the interior of the liquid is impossible. Evaporation proceeds silently without ebullition as the temperature rises up to a certain point, and then a very striking transformation occurs. The meniscus separating the vapour and liquid grows indistinct and completely disappears; the substance appears no longer to exist in two distinct states; the whole mass has become apparently homogeneous and completely vaporised. The temperature at which this occurs for any substance is called the *critical temperature* for that substance, and the corresponding pressure and specific volume are similarly termed the *critical pressure* and *critical volume.*

This silent evaporation of a liquid in a sealed tube and the apparently sudden vaporisation of the whole mass at a certain temperature was first shown by Cagniard de La Tour.[1] The apparatus consisted simply of a bent tube, one end A of which contained air (Fig. 105) to indicate the pressure, and the other end B con-

[1] Cagniard de La Tour, *Annales de Chimie et de Physique,* 2e, toms. xxi, xxii. xxiii., 1822-23.

tained the liquid to be experimented on. The space between A and B was filled with mercury. If, in addition, both arms are graduated, the critical pressure and volume may be determined simultaneously. At low temperatures the vapour pressure may be less than that caused by the air in A and the column of mercury, and there will be no vapour in B. As the temperature of B is raised the vapour pressure increases, a bubble of vapour forms in B, and the mercury is forced into the other arm, compressing the air in A. The surface of demarcation between the liquid and vapour gradually flattens as the temperature rises, and at a certain temperature it loses its curvature altogether and disappears. The whole space above the mercury in B now appears to be filled with vapour only, although the total volume may be only three or four times the initial volume of the liquid.

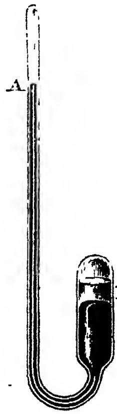


Fig. 105

This transformation might have been suspected as a possibility arising from the diminution of surface tension with rise of temperature. For it is well known that the surface tension of a liquid diminishes with rise of temperature. The surface tension under consideration here is that of a liquid in contact with its own saturated vapour (this probably is the case always presented), and if it goes on diminishing, a temperature will presumably be possible at which it will vanish. We will then have no capillarity and no surface of separation between the liquid and vapour, the physical meaning of which is probably that they mix in all proportions, or that the vapour is completely soluble in the liquid. It is not to be concluded, however, that the liquid and vapour become identical in all respects at this point; such identity may or may not exist; the only inference we can draw when the surface tension vanishes is that the vapour dissolves in the liquid in all proportions. That something of this nature actually occurs is suggested by observation of the phenomenon. As the temperature rises the meniscus which forms the upper boundary of the liquid gradually grows more flat and indistinct until it ultimately vanishes. A peculiar undulating appearance is then presented throughout the mass, as if the liquid and vapour were mixing through each other. On cooling down again a mist suddenly appears about the middle of what was an apparently empty tube. This rapidly spreads throughout the whole interior and suddenly vanishes, leaving the lower part of the tube filled with liquid, a distinct meniscus separating it from the vapour-filled space above.

The matter may also be regarded from another point of view. Thus, as the temperature rises, the absolute vapour density increases, while that of the liquid diminishes, and therefore it is possible that a temperature may be attained at which the density of the liquid is equal to that of the vapour. This temperature, in fact, is the critical temperature, and from the equality of density of the vapour and liquid at this point Dr. Ramsay [1] inferred that the phenomena presented in the experiment of Cagniard de La Tour found their explanation. Three years later M. Jamin [2] put forward the same theory. From this point of view it would appear that when two substances (or at least a liquid and its vapour) have the same density there should be no surface tension between them; or, in other words, they should mutually mix in all proportions. This, however, by no means follows as a consequence. Two substances may have the same density without possessing the property of mixing (otherwise Plateau's beautiful experiment could never have been made). The property of mixing depends on the molecular attraction rather than on equality of density, and therefore the theory of Ramsay and Jamin fails to lead us any further than its first postulate—namely, the equality of density. If the molecular attraction as well as the density be the same throughout the liquid and vapour, there will be no distinctive difference between the two states at the critical temperature, and the whole mass may be regarded as simply vaporised, as Cagniard de La Tour supposed.

The critical temperature of a liquid is most easily determined by filling a strong glass tube with it and then boiling off about one-third the liquid and sealing up. The tube is now about two-thirds full of the liquid, and contains no air. On gradually heating, the meniscus gradually flattens and ultimately disappears. On cooling slowly, the liquid reappears again, and the mean of the two observations may be taken as the critical temperature.[3] The critical pressure is much more difficult to estimate. For this purpose the tube containing the liquid must be connected with a manometer, preferably filled with nitrogen, as the compressibility of

[1] Wm. Ramsay, *Proc. Roy. Soc.*, vol. xxx. p. 326, 1880.

[2] Jamin, *Journal de Physique*, 2^e, tom. ii. p. 389, 1883; *Annales de Chimie et de Physique*, 4^e, tom. xxi. p. 208; *Phil. Mag.*, July 1883.

[3] Wm. Ramsay (*Proc. Roy. Soc.*, vol. xxx. p. 323, 1880) found that the temperature at which the meniscus disappeared varied with the quantity of liquid in the tube, being greater the greater the quantity of liquid originally taken. Thus with methyl-formate, two-thirds filling the tube, the meniscus disappeared at 221°·5 C.; with a greater quantity of liquid in a similar tube the meniscus vanished at 228° C.; and with a less quantity at 215° C. It is possible, however, that these inconsistencies may be due to impurities, or to the difficulty of ascertaining the precise temperature inside a thick *glass* tube.

this gas at high pressures has been very carefully investigated by M. Amagat[1] (see p. 403).

Impurity, or dissolved air or other gas, may lead to a considerable change in the critical temperature, so that discrepancies may arise in different experiments even by the same observer. The following table shows the rough results obtained by Cagniard de La Tour:—

Liquid.	Crit. Temp.	Pressure in Atmos.	Ratio of Volume of Vapour to Volume of Liquid.
	° C.		
Ether	175	38	$2\frac{6}{7}$
Alcohol . .	248	119	3
Carbon-bisulphide	254	71	$2\frac{1}{2}$
Water . . .	362	Indeterminate[2]	4

Similar determinations were made by Drion[3] for sulphurous acid and ethyl chloride.

210. Liquefaction of Gases.—The experiments of Cagniard de La Tour and Drion show that at a certain temperature all visible distinction between a liquid and its vapour ceases. Above this temperature, then, it would appear to be impossible to liquefy the vapour by pressure alone. At least compression will produce no visible condensation or

[1] The specific heats of some substances near their critical points have been determined by P. de Heen (*Beiblätter der Physik*, No. IX., 1888). The method of cooling was used. For ether, amylene, and bromide of ethyl there was at the critical temperature a sudden diminution in the specific heat.

	Temp.	Sp. Heat.
Ether .	185	0·547
	180	1·041
Amylene . .	175	0·773
	170	1·500
Bromide of ethylene	220	0·233
	215	0·852

With aldehyde, which, however, decomposed, there were no analogous phenomena.

The author infers from the behaviour of the former substances that as the critical temperature is reached the gas-forming molecules relinquish their supposed closed curves, and describe rectilinear paths.

[2] Water vapour attacks glass at high temperatures and renders it opaque, so that the disappearance of the meniscus cannot be seen, and explosion soon occurs under the joint action of corrosion and pressure. In order to overcome these difficulties, La Tour added to the water some substance which prevented the attack on the glass, but the critical point of this mixture is not that of pure water.

[3] Ch. Drion, *Annales de Chimie et de Physique*, 3e, tom. lvi. p. 5, 1859.

formation of a liquid with a meniscus separating it from the vapour above, such as occurs when the temperature is lower than the critical temperature. For the visible condensation of a gas, then, the temperature must be reduced below the critical temperature, and then by applying sufficient pressure liquefaction may be produced.

Faraday[1] first succeeded in liquefying by pressure, at the ordinary temperature of the air, chlorine, and several other gases previously unknown in the liquid state. A few years later Thilorier[2] obtained solid carbonic acid, and found that the coefficient of expansion of the liquid was greater than that of a gas. Faraday[3] published a second memoir on the effects of cold and pressure on gases, which greatly extended the knowledge of the subject. Subsequently Regnault and Pouillet carefully examined the change of volume of a few gases when subject to pressures up to 20 atmospheres, and Natterer[4] carried the inquiry up to the enormous pressure of nearly 3000 atmospheres. The results of the latter experiments were valuable at the time, but the method was not free from objection in point of accuracy.

The great problem of the time was the liquefaction of what were termed the permanent gases—oxygen, hydrogen, etc. It was in pursuit of this inquiry that Andrews was led to his classic investigations on the behaviour of carbonic acid gas, and other substances, under pressure at different temperatures.

211. Andrews's Experiments.—In 1863 Dr. Andrews wrote as follows:—"On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° F., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° F. no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."[5]

The apparatus[6] employed in these investigations is represented in Figs. 106-8. The gas to be compressed was introduced into a glass tube *af* (Fig. 106), having a capillary bore from *a* to *b*, and a diameter

[1] Faraday, *Phil. Trans.*, pp. 160-189, 1823.
[2] Thilorier, *Ann. de Chimie*, 2e, tom. lx. p. 427, 1835.
[3] Faraday, *Phil. Trans.*, 1845, p. 155.
[4] Natterer, *Pogg. Ann.*, vol. xciv. p. 436, 1855.
[5] Miller's *Chemical Physics*, 3rd edit., p. 328.
[6] Andrews, *Phil. Trans.*, 1869, part ii. p. 575.

of about 2·5 mm. from b to c. The diameter of the third part cf was about 1·25 mm. The gas was first carefully dried and then passed for several hours through the tube open at both ends, in order to expel all air. Even after passing the current of gas through the tube for twenty-four hours, it was found that the residual air could not be reduced to less than $\frac{1}{500}$ to $\frac{1}{1000}$ of the entire volume of the carbonic acid, and consequently in discussing the results of the experiment the presence of this small quantity of air must be taken into account.

The capillary end a of the tube was finally sealed, and the other end was temporarily closed and plunged below the surface of pure

Fig. 106.

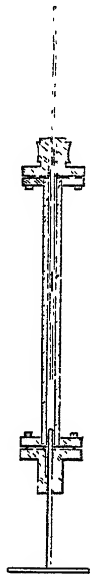


Fig. 107.

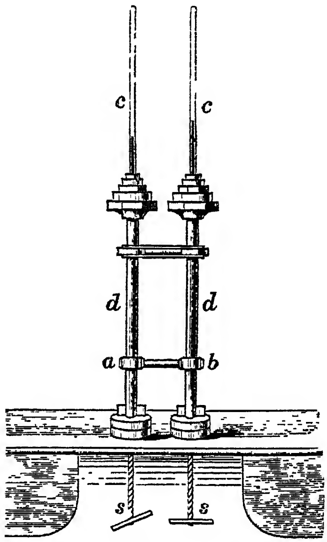


Fig 108.

mercury. The lower end while under the surface of the mercury was opened, and the tube was slightly heated so as to expel a little of the gas. On cooling contraction occurred, and a short column of mercury entered the tube. The tube, with its lower end still under mercury, was then placed under the receiver of an air pump, and a partial vacuum was formed till about one-fourth of the gas had escaped from the tube. On restoring the pressure, a column of mercury entered and occupied the place of the expelled gas. By cautiously exhausting this column of mercury could be rendered any length required. The tube was previously calibrated by means of a moving thread of mercury, and the volume of the gas at 0° C. and 760 mm. was calculated. The

capillary tube was also calibrated with great care by weighing a column of mercury whose length in different parts of the tube was accurately measured.

Two massive brass flanges (Fig. 107) were firmly attached to the ends of a strong copper tube, and by means of these flanges two brass end-pieces were securely bolted to the ends of the copper tube, and the connections were made air-tight by leather washers soaked in lard heated in vacuo. The lower end-piece carried a steel screw 180 mm. long and 4 mm. in diameter, which easily held a pressure of more than 400 atmospheres. A similar end-piece attached to the upper flange carried the glass tube containing the gas.

The apparatus before being screwed up was filled with water, and the pressure was produced by screwing the steel plunger into the water. In order to register this pressure a similar tube containing air was placed beside the experimental tube which contained the gas (Fig. 108), and lateral communication between the two was established through a connecting tube *ab*, so that equality of pressure was maintained in both. The air-tube was also furnished with a steel screw, and either screw, or both, might be used in altering the pressure. The gas under examination could be kept at any required temperature by jacketing the tube with a bath or a freezing mixture if necessary.

The actual pressures were not deduced by Andrews, as he was not furnished with sufficient experimental data on the deviations of air from Boyle's law, and the pressures he speaks of are those calculated on the apparent compression of the air in the second tube; but these are approximately correct as the deviation from Boyle's law is small, as is also the change of internal volume of the tube under pressure. Andrews [1] found that no permanent enlargement of the glass tubes took place even when kept under high pressure for a long time, and that no oxidation of the mercury occurred in the air-tube during a period of two months' active work, and that after standing for five months all was found correct.

From the results of these experiments Andrews plotted the curves shown in Fig. 109.

At a temperature of $13^{\circ}\cdot 1$ C. liquefaction of the gas commenced at a pressure of 48·89 atmospheres, as measured by the compression of the air in the tube. This point could not be determined by direct observation, inasmuch as the smallest visible quantity of liquid represented a column of gas at least 2 or 3 mm. in length. It was, however, determined indirectly by observing the volume of the gas at $0^{\circ}\cdot 2$

[1] Andrews, *Phil. Trans.*, part ii. p. 421, 1876.

or 0°·3 above the point of liquefaction, and calculating the contraction the gas would sustain in cooling down to the temperature at which liquefaction began. A slight increase of pressure was required even in the early stages to carry on the process of liquefaction, the air-gauge indicating an increase of about $\frac{1}{4}$ atm. during the condensation of the first and second thirds of the carbonic acid. This rise of pressure during condensation may be explained by the presence of the trace of air ($\frac{1}{500}$) already referred to, for during liquefaction increase of pressure is necessary in order to compress it. This small quantity of air disturbed the liquefaction in a marked manner when nearly the whole of the acid was liquefied, and when its volume relatively to that of the uncondensed carbonic acid was considerable. It resisted for some time absorption by the liquid; but on raising the pressure to 50·4 atmospheres, it was entirely absorbed. If the carbonic acid had been quite pure the part of the curve for 13°·1, representing the fall from the gaseous to the liquid state, would doubtless have been straight throughout its entire course, and parallel to the lines of equal pressure.

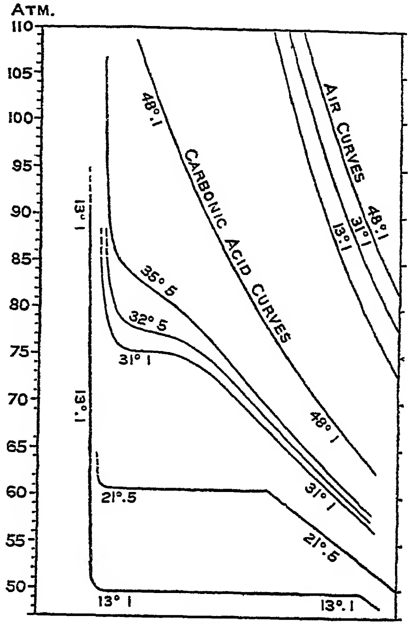


Fig. 109.

The curve for the temperature 21°·5 agrees in general form with that for 13°·1. At 13°·1 the volume under a pressure of 49 atm. is little more than $\frac{3}{5}$ of that which a perfect gas would occupy under the same conditions. After liquefaction carbonic acid yields to pressure much more than ordinary liquids, and the compressibility appears to diminish as the pressure increases, and the high rate of expansion by heat noticed by Thilorier is fully confirmed by these experiments.

The next series of experiments was made at 31°·1, or 0°·2 above the temperature at which, by compression alone, carbonic acid is capable of assuming visibly the liquid form. This point was found after repeated trial to be 30°·92 C., or 87°·7 F. For a few degrees above this temperature an increase of pressure produces a rapid change of volume, and

when the gas is reduced to the volume at which it might be expected to liquefy no visible separation of the carbonic acid into two distinct conditions of matter occurs. By varying the pressure, or temperature, but always keeping the latter above 30°·92, the great changes of density which occur about this point produce flickering movements, resembling in an exaggerated form the appearances exhibited during the mixture of liquids of different densities, or when columns of heated air ascend through colder strata. The curve for 31°·1 shows that the volume diminishes regularly, but much faster than if the substance obeyed Boyle's law, till a pressure of about 73 atmos. is reached. The diminution of volume then goes on very rapidly, a reduction of nearly one-half taking place, while the pressure is increased from 73 to 75 atmos. The fall is not, however, abrupt, as in the case of the formation of the liquid at lower temperatures, but a steady increase of pressure is necessary to effect it. During this fall there is no evidence of the presence of liquid in the tube, no heterogeneity can be detected in the whole mass. Beyond 77 atmos. the substance yielded much less to pressure than before, its volume being now reduced to that which liquid carbonic acid should occupy at this temperature.

The curve for 32°·5 closely resembles that for 31°·1. The fall, however, is less abrupt, and in the curve for 35°·5 the fall is still greatly diminished, and has nearly lost its abrupt character. The range of pressure here extended from 57 to 107 atmos. It is most considerable from 76 to 87 atmos., where an increase of $\frac{1}{7}$ the total pressure produced a reduction to half the volume. At 107 atmos. the volume is that which the liquid would occupy at this temperature, according to the expansion of the liquid by heat.

The curve for 48°·1 is very interesting. The abrupt fall shown in the lower temperature curves has disappeared, and the curve approximates to that which would represent the change of volume of a perfect gas. At the same time the compression is much less than that indicated by Boyle's law. Under 109 atmos. the substance is rapidly approaching the liquid volume. Experiments above 48°·1 were not made; but it is clear that as the temperature rises the curve will continue to approach that of a perfect gas.

Experiments were made at much higher pressures, and the substance was made to pass without break or interruption from what is universally regarded as the gaseous state to what is, in like manner, regarded as the liquid state. Take, for example, carbonic acid at 50°, or at a higher temperature, and let the pressure be increased to 150 atmospheres. In this process its volume will steadily diminish as the pressure increases. When the full pressure has been attained, let the

temperature be allowed to fall to the ordinary temperature of the atmosphere. During the whole of this process no breach of continuity occurs. The substance at the beginning is what is ordinarily regarded as a gas, and at the end it is liquid carbonic acid, and nowhere during the process is there any abrupt change of volume or sudden evolution of heat. The closest observation fails anywhere to detect change of condition in the substance, nor is there any evidence that at any time one part of it is a gas and the other a liquid. The process of compression and cooling might also be conducted simultaneously, if care be taken to avoid having the pressure less than 76 atmos. when the temperature is 31°.

These properties are not peculiar to carbonic acid. They are generally true of all substances which can be obtained as gases and liquids. Nitrous oxide, hydrochloric acid, ammonia, sulphurous acid, etc., all exhibit critical points and rapid changes of volume with flickering movements when the pressure is changed in the neighbourhood of these points.

Below the critical temperature, when the pressure is increased to a certain value, the substance suddenly changes from the gaseous to the liquid state; but no such abrupt change occurs above this temperature, the substance being gradually reduced to the liquid volume. The change from the gaseous to the liquid state below the critical temperature is abrupt, like the change from the liquid to the solid state in crystalline substances, whereas above the critical temperature it is gradual, like the solidification of amorphous substances.

212. On the State of Matter near the Critical Point.—The question now arises for consideration as to the state of a body at or a little above its critical point. Is it gaseous or liquid, or a mixture of the two states? When carbonic acid gas is compressed at temperatures above 31° C. no visible evidence of liquefaction is obtained, even when the compression is pushed up to the point at which the liquid volume is attained. In this case, then, does the substance continue throughout in the gaseous state, or does it liquefy in the whole or in part, or are we presented with a new state of matter? Such are the questions raised by Andrews, and since they were first proposed they have been the subject of much discussion and inquiry. If carbonic acid gas at 100° C., for example, or any higher temperature, is compressed, few would hesitate to declare that the gaseous state is maintained throughout the compression, just as when hydrogen or nitrogen is subjected to great pressures at ordinary temperatures.

On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31° C., the rapid change of volume

which occurs during a certain period of the experiment would lead to the conjecture that liquefaction, total or partial, actually takes place, although optical tests fail to detect it. Against this view it might be urged that during this period of rapid change of volume, increase of pressure is always necessary for diminution of volume, and this is opposed to the ordinary laws of the liquefaction of saturated vapours. Furthermore, the higher the temperature the less marked this period of rapid change becomes, until it ultimately disappears.

In the opinion of Andrews the answer to the question is to be found in the intimate relations which exist between the gaseous and liquid states of matter. These he regards as only widely-separated forms of the same condition of matter, which may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. Thus at high temperatures and low pressures the substance approximates to the condition of an ideal gas obeying Boyle's law. Increase of pressure and reduction of temperature decrease the mean free path and kinetic energy of the molecules, and the substance begins to deviate sensibly from Boyle's law. It commences to acquire the properties of the liquid, and gradually loses the distinctive properties of the so-called perfect gas. The gas and liquid then are, in the opinion of Andrews, "only distant stages of a long series of continuous physical changes."

In the opinion of MM. Cailletet and Colardeau,[1] however, and other French physicists, the liquid state persists after the critical point has been passed. At the critical point the liquid dissolves the vapour in all proportions. For this reason the surface of separation disappears in the experiment of Cagniard de La Tour, and the tube becomes apparently empty. In support of this view the following experiment is quoted. Iodine possesses the property[2] of dissolving in liquid carbonic acid and colouring it. It does not, however, dissolve in the vapour. A small quantity of iodine was consequently deposited by vaporisation on the upper end of the tube in which carbonic acid gas was compressed to liquefaction, and a thin layer of sulphuric acid protected the mercury from the action of the iodine. When the liquid carbonic acid attained the level of the iodine it dissolved a portion of it, and became of a rosy violet colour. On raising the temperature to 31° C. the meniscus disappeared as usual, while the colour remained in all that part of the tube which was previously occupied by the liquid. The colour did not

[1] Cailletet and Colardeau, *Journal de Physique*, tom. viii., 1889 ; *Ann. de Chimie et de Physique*, 6e, tom. xviii., Oct. 1889.

[2] Cailletet and Hautefeuille, *Comptes Rendus*, tom. xcii. p. 840, 1881.

spread through the whole mass, but was restricted to the same region as before. From this it would appear that the liquid is not really converted into vapour, as Cagniard de La Tour supposed, but that the meniscus alone disappears. The part which was liquid still retains the power of holding iodine in solution, while the vapour above has not yet attained the property of dissolving iodine, for in the upper part of the tube it is in contact with the deposit of iodine, but remains without action upon it.

Analysis by the spectroscope indicated that the iodine was still in solution, and not suspended in the lower part of the tube. The absorption spectrum of iodine in solution is very different from that of iodine vapour; but as the critical point was passed the absorption spectrum of the coloured CO_2 showed no change.

The same authors also attacked the problem from another point of view. If the substance is altogether vaporised at the critical point, then as the temperature is raised beyond the critical point the tube will be filled with a non-saturated vapour, and it was inferred that the curve connecting its pressure and temperature should be unique (being that of a gas near its condensing point), and should therefore be independent of the quantity of liquid present just before the meniscus disappears. If, on the other hand, the liquid state still persists, vaporisation will go on beyond the critical point just as before, and the pressure at any temperature will depend on the quantity of liquid present when the meniscus is about to vanish. Fig. 110 shows the result of experiments made with different initial quantities of liquid. The part OM indicates the pressure of the saturated vapour as the temperature rises to the critical point. Above this point the curve is not unique, but depends on the quantity of liquid present when the meniscus is about to vanish.[1] The branches MD, ME, etc., correspond to the cases in which the liquid occupied different fractions of the total length of the tube at the moment of disappearance of the meniscus. Hence the portion of the pressure temperature curve above the critical point depends on the quantity of liquid present when this point is just reached, and this seems to favour the idea, proposed by Ramsay in 1880 and Jamin in 1883, that the liquid persists beyond the critical point, and that the meniscus alone has vanished. The vanishing of the meniscus means that equality of molecular attraction in the liquid and vapour has been established. It does not necessarily follow that equality in density has also been

[1] It is possible that this may arise from the presence of impurities, and the difficulty of securing a uniform temperature inside a thick glass tube, or it may depend on the pressure (see further note on p. 398).

attained, and conversely equality of density alone does not lead to identity of molecular attraction and the vanishing of the meniscus. Equality of density alone was assumed by Ramsay and Jamin, so that at the critical point the liquid could swim freely on the vapour. M. Jamin[1] expected also that with increased pressure above the critical point the vapour would become more dense than the liquid, and that the latter would consequently rise to the top of the tube and float on the vapour. This reversal could not be obtained after

Steam-line for water.

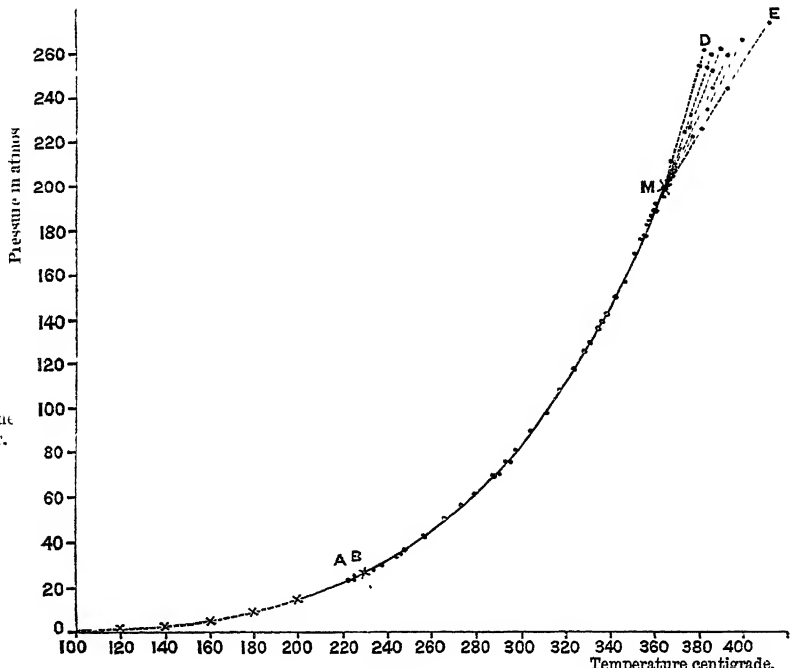


Fig. 110.

repeated trial by M. Cailletet,[2] and although such an extraordinary result might be possible, yet it is certainly not to be reasonably demanded. In order that it should occur (admitting the simultaneous existence of the two states above the critical point), the compressibility of the vapour above the critical point should be greater than that of the liquid, and this might or might not be the case.

The mutual solubility of two substances depends on the temperature and pressure. M. Duclaux[3] has shown that two liquids which

[1] Jamin, *Journal de Physique*, 2e, tom. ii. p. 389, 1883.
[2] Cailletet, *Journal de Physique*, 1e, tom. ix. p. 192, 1880.
[3] Duclaux, *Journal de Physique*, 1e, tom. v. p. 13, 1876.

do not mutually dissolve each other in all proportions may be made to do so by suitably altering the temperature. Thus amylic alcohol and ordinary alcohol diluted with water when shaken together in a tube at ordinary temperatures do not mix completely, but settle into two layers with a distinct surface of separation. As the tube is gradually warmed, however, a temperature is reached at which the meniscus flattens and disappears, and the liquids mix completely, forming an apparently homogeneous fluid. On cooling again, as this temperature is approached, striæ and undulations appear, as in the experiment of Cagniard de La Tour. At this temperature the liquids have not the same density; the property of mutual solubility alone has been acquired. The conclusion of Cailletet and Colardeau is therefore that the critical point is not necessarily the point at which the density of the vapour is equal to that of the liquid, but the point at which the vapour and liquid mutually dissolve each other in all proportions. From this point of view the liquid may exist in solution in its own vapour, and when a gas is highly compressed the liquid may be present although invisible. It only becomes visible when the temperature is below that of the critical point. That liquid carbonic acid really exists in solution in the gas at 40° C. under a pressure of from 80 to 100 atmospheres, M. Cailletet considers confirmed by the fact that the substance in this state dissolves iodine.

The simultaneous existence of the two states above the critical point does not, however, appear to have been sufficiently proved. All experiments prove that as this point is approached the density of the liquid approximates to that of the vapour. In the upper and lower parts of the tube we have then the same substance at the same temperature, pressure, and density, and when the meniscus disappears they have further the same molecular attraction or are mutually soluble, and there seems no reason for the supposition that the substance in the upper part of the tube is in a different state of molecular aggregation from that in the lower. Mr. Hannay[1] describes experiments in which the liquid was coloured and the vapour above it colourless, but on passing the critical point the whole became coloured, showing that mutual diffusion occurred. This of course does not prove that the liquid state may not persist beyond the critical point; but, on the other hand, the experiment cited by M. Cailletet as to the solubility of iodine in highly compressed carbonic acid does not prove that liquid carbonic acid is present. For according to his own showing the solubility of one substance in another depends on the temperature and pressure, so that although carbonic acid gas may not dissolve

[1] J. B. Hannay, *Proc. Roy. Soc.*, vol. xxxiii. p. 294, 1881.

iodine at low pressures, this property may be acquired by it at other pressures and temperatures, and even though the vapour in the upper part of the tube did not acquire this property at the critical point, all that is proved is that the matter occupying the lower part of the tube still retains the power of *holding in solution* the iodine already dissolved in it.

The difficulty is probably fostered by the vague use of the terms liquid and vapour in this case. The essential difference between a liquid and vapour, besides that of aggregation, is entirely one of the length of the mean free path of the molecules. As the temperature and pressure increase the mean kinetic energy of the molecules increases and the mean free path in the vapour diminishes, so that when the critical point is reached there appears to be no reason why both these quantities should not be the same in the upper and lower parts of the tube, that is, uniformity of state is established throughout the mass; but as to whether this state is to be called liquid or vapour, or a mixture of both, depends merely on a choice of terms.

213. On the Determination of the Critical Constants.—The physical constants which characterise the critical state of matter have become of considerable importance in the determination of the mathematical functions which represent the thermal and mechanical properties of fluids, and which establish the relations between the liquid and gaseous states. The accurate determination of the three critical constants for various substances is consequently a matter of importance. Of these the critical temperature is the most easily determined, for by employing as heaters the vapours of pure liquids boiling under a constant pressure, which can be adjusted at pleasure, the temperature can be regulated with considerable nicety, and is easily measured.

The critical pressure may also, as a rule, be determined without very much difficulty, provided that the substance is obtained perfectly pure,—a matter of prime importance. In the case of substances which attack mercury at high temperatures the ordinary method of operation requires modifications, which render the calculations more laborious, but otherwise the difficulty is not greatly increased.

The estimation of the critical volume, even when the substance is perfectly pure and without action on mercury, is a matter of much greater difficulty. In order to secure a correct reading of the critical volume it is necessary that the substance should be exactly at the critical temperature. A very small alteration of temperature, such as $0^\circ{\cdot}1$ C., at, or just below, the critical point, produces a considerable alteration in the volume, and for this reason a small error in the temperature leads to a considerable error in the volume. The main

object is therefore to bring the substance exactly to the critical temperature. Professor Sidney Young[1] takes the substance to be in this state when, on rapidly increasing the volume somewhat above the critical volume, the fall of temperature due to expansion causes a momentary separation of the liquid and vapour. In order to determine the critical volume this temporary mark of division is noted, and the volume then slightly diminished. After a few minutes the temperature becomes constant, and the volume is again increased slightly but rapidly, and the position of the mark of division of liquid and vapour again noted, this being now nearer the top of the tube. Proceeding in this way, it is possible, under favourable conditions, to make the substance occupy such a volume that a very slight but rapid expansion gives a temporary mark of division of liquid and vapour almost exactly at the top of the tube. This volume Professor Young takes as the critical volume.

Case of water.

In the case of substances, such as water, which attack glass at high temperatures, these methods cannot be applied. The method adopted by MM. Cailletet and Colardeau[2] in the case of water was founded on the observation of the vapour pressure curve when the liquid was enclosed in a strong steel tube. If a suitable quantity of the liquid be taken in the tube the vapour pressure will be unique up to the critical point, but beyond this point the course of the curve will depend on the quantity of liquid present when the critical point is approached (Fig. 110). By starting with different quantities of liquid in the tube, the point at which the vapour pressure curve begins to branch can be determined, and the critical constants thence deduced. The same method may be employed to determine the critical constants of any other substance, the inside of the tube being coated with platinum, or some other substance, to avoid attack.

The apparatus of Cailletet and Colardeau is shown in Fig. 111. The tube FD which contained the water was made of steel sufficiently strong to resist the pressures experienced during the experiments. This tube was heated directly in a bath VV′, and by means of a flexible steel tube ABC it communicated with another similar and equal steel tube ET, which communicated with a hydrogen manometer M and a pump by which water was forced into both. The pressure of the vapour in FD is transmitted to the manometer by means of this water and the thread of mercury in the tube DABCE. An insulated platinum wire penetrates the wall of the tube ET at S, and when

[1] S. Young, *Phil. Mag.*, vol. xxxiii. p. 181, 1892.

[2] Cailletet et Colardeau, *Comptes Rendus*, tom. cxii. p. 563, 1891; and *Ann. de Chimie et de Physique*, 6e, tom. xxv. p. 519.

the mercury rises to this level, so as to come into contact with it, an electric circuit is closed and an electric bell is set ringing. By this means the level of the mercury in ET can be kept exactly at S, and consequently the space DF occupied by the liquid and vapour can be kept constant. When the temperature rises the vapour pressure increases, and the mercury is forced through ABCE and rises into contact with the platinum wire at S, and sets the bell in motion. The pump is then placed in action till the ringing just ceases. A second platinum wire penetrates the wall of TE, insulated at S′, some centimetres above S, and this is in connection with another bell, so

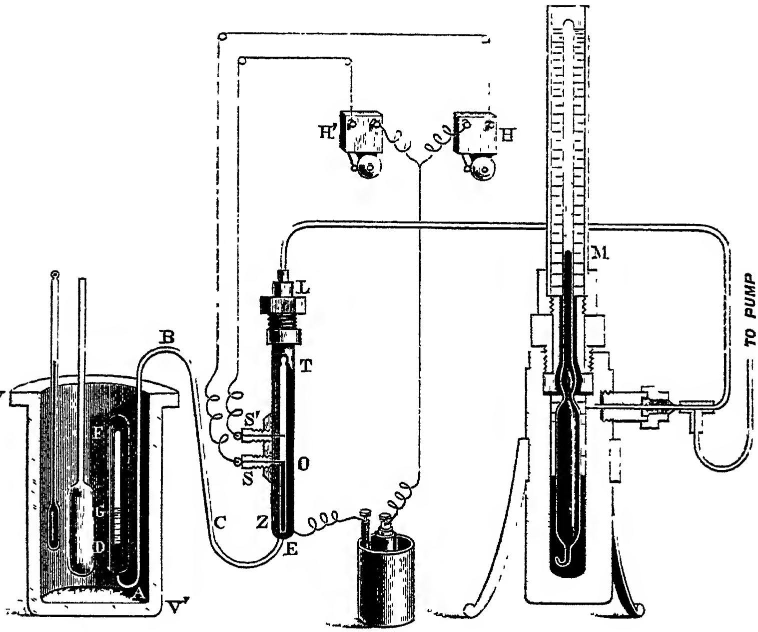


Fig. 111.

that if the expansion of the vapour is rapid, or the action of the pump too slow, the mercury rises to S′ and the second bell rings. This gives warning that the vapour is on the point of expelling all the mercury from the reservoir, and this of course must be avoided.

The liquid first employed in the bath was mercury, the boiling point of which is below the critical temperature of water. For higher temperatures a bath of equal parts of the nitrates of soda and potash was used. This mixture is notably more fusible than either constituent, becoming liquid at 220° C., and can be used easily up to above 400° C. The bath was heated by a gas-burner,

which was controlled so as to give a stationary temperature. The following results were obtained for the pressure of saturated water vapour :—

Temperature.	Pressure.	Temperature.	Pressure
° C.	atm.	C.	atm.
225	25·1	300	86·2
230	27·5	305	92·2
235	30·0	310	99 0
240	32·8	315	106·1
245	35·5	320	113·7
250	39·2	325	121·6
255	42·9	330	130·0
260	46·8	335	138·8
265	50·8	340	147·7
270	55·0	345	157·5
275	59·4	350	167·5
280	64·3	355	178·2
285	69·2	360	188·9
290	74·5	365	200·5
295	80·0		

The curve of vapour pressure branches at 365° C., which is therefore the critical temperature of water substance, the corresponding pressure being 200·5 atmos. (see Fig. 110).

214. Distinction between Gases and Vapours.—Previous to the experiments of Andrews there was no clear distinction between gases and vapours. In general, substances which assumed the gaseous condition at ordinary temperatures were termed gases, while those which assumed the condition of a liquid at the ordinary temperatures of the air were termed vapours when in the gaseous state. Thus ether in the gaseous state was termed a vapour, whereas sulphurous acid was called a gas, yet these substances, from the present point of view, are both vapours—one derived from a liquid boiling at 35° C., and the other from a liquid boiling at −10° C. The distinction between gases and vapours was thus determined by the trivial circumstance of the boiling point of the liquid being lower or higher than the ordinary temperature of the atmosphere. Such a distinction may have advantages for ordinary reference, but it is without scientific value. A criterion for scientifically distinguishing between a gas and a vapour is afforded, as Andrews pointed out, by the critical temperature. Thus a substance can exist partly in the liquid and partly in the gaseous state, or as a liquid and vapour in contact, only at temperatures below the critical temperature. Above the critical temperature it is impossible to compress the

substance so that part of it may visibly assume the liquid state while the remainder exists as a vapour. For this reason a vapour may be defined as a gaseous substance, which may be in the whole or in part compressed into the liquid state—that is, a gaseous substance at a temperature lower than the critical temperature. On the other hand, a gas is a substance at a temperature higher than its critical temperature.

According to this definition, any substance may be a gas or a vapour according to its temperature. A gas cannot be changed into a liquid by pressure alone, but a vápour may be changed by pressure into the liquid state, and may exist in presence of its own liquid. Thus carbon dioxide is a gas above 31° C., and a vapour at lower temperatures.

215. Critical Point of a Mixture.—In his later experiments Andrews[1] proved that the presence of a so-called permanent gas, such as air, lowered in a marked manner the critical temperature of a liquefiable gas, such as carbonic acid. Thus when three volumes of carbonic acid gas were mixed with four of nitrogen no liquefaction took place at any pressure until the temperature was reduced to −20° C. The addition of even $\frac{1}{10}$ of its volume of air or nitrogen to carbonic acid lowers the critical temperature several degrees.

An extremely important observation was made by M. Cailletet[2] in this department. A mixture of five parts of carbonic acid with one of air was compressed at such a temperature that liquefaction was produced. On gradually increasing the pressure at constant temperature the meniscus of the liquid faded, and at a certain pressure disappeared (cf. p. 379). On diminishing the pressure again the liquid reappeared, and the pressure at which this occurred was lower the higher the temperature, as shown by the following table:—

Pressure (atm.) . .	132	124	120	113	110
Temperature . .	5°·5 C.	10°	13°	18°	19°

At 21° C., however, the gas did not liquefy under a pressure of 400 atmospheres.

The disappearance of the liquid carbonic acid on increasing the pressure is very plausibly explained from Cailletet's point of view that the solubility in the liquid of the gas, or mixture of gas and vapour, occupying the upper part of the tube, increases with the pressure, and

[1] Andrews, *Proc. Roy. Soc.*, vol. xxiii. p. 514, 1875.

[2] Cailletet, *Comptes Rendus*, tom. xc. p. 210; and *Journal de Physique*, 1e, tom. ix. p. 192, 1880.

at a certain pressure they will mix in all proportions, and the surface of separation will disappear at this point.[1]

Further investigations of the critical points of mixtures have been made by Ramsay, Pawlewski, Ansdell, and Dewar. According to Pawlewski,[2] the critical point of a mixture of two substances belonging to the same class of organic compounds should be intermediate between that of the constituents, and divide the interval between the critical temperatures of the constituents in a proportion measured by the percentage composition of the mixture. Thus Dr. Ramsay found that the critical temperature of a mixture of equal weights of pure benzene and ether was half-way between those of the constituents. According to the experiments of Mr. G. Ansdell,[3] this law is not accurately fulfilled by mixtures of hydrochloric and carbonic acids. If the law held generally, then the critical temperature of any substance, such as hydrogen or nitrogen, could be determined by noting the critical temperature of a definite mixture of it with some other substance, such as carbonic acid whose critical temperature is known.

In the experiments of Professor Dewar[4] on mixtures of carbonic acid with other substances, liquefaction appeared to set in at temperatures above the critical temperature of the acid. The presence of the second substance thus appeared to raise the critical point. This may perhaps arise from the formation of some new compound under particular conditions of temperature and pressure. These experiments are very interesting. Thus carbon dioxide in presence of bisulphide of carbon liquefied under 49 atmos. at 19° C., and floated on the convex surface of the bisulphide. At 35° C. liquefaction took place under 78 atmos., and at 40° C. under 85 atmos. At 58° C. liquefaction seemed to occur at 110 atmos. On keeping the temperature at 47° C. and gradually increasing the pressure, the upper surface of the liquid carbon dioxide disappeared under 110 atmos., as in Cailletet's experiment, and reappeared on reducing the pressure to 75 atmos.

In presence of chloroform at 28° C. the carbon dioxide liquefied under a pressure of 25 atmos., and on increasing the pressure to 50 atmos. the two liquids mixed completely. At 35° C. liquefaction set in under a pressure of 55 atmos., and the CO_2 mixed rapidly with the chloroform on standing.

[1] This question has been attacked thermodynamically by M. Duhem (*Journal de Physique*, tom. vii. p. 158, 1888), who shows that the experimental results follow from the thermodynamic potential of the system.

[2] *Berichte*, No. IV., 1882.

[3] G. Ansdell, *Proc. Roy. Soc.*, vol. xxxiv. p. 113, 1882.

[4] James Dewar, *Proc. Roy. Soc.*, vol. xxx. p. 538, 1880.

In presence of benzole the carbonic acid liquefied at 18° C. and a pressure of 25 atmos.; and at the moment of liquefaction the surface of the benzole was violently agitated, the liquid carbonic acid falling through it in an oily stream, and mixing with it completely up to a certain point. It then collected on the surface in a distinct layer as further condensation proceeded, but on standing for about five minutes the line of separation disappeared, and the two liquids formed an apparently homogeneous mixture. On releasing the pressure the carbonic acid boiled away rapidly from the benzole. At 35° liquefaction occurred under 35 atmos.; but in this case the liquid carbonic acid did not fall through the benzole as before, or appear to be nearly so soluble in it. At 52° C. and 70° C. liquefaction occurred under 60 and 85 atmos. respectively, and in each case the two liquids mixed —in the former on standing, and in the latter rapidly. Similar results were obtained in presence of ether and nitrous oxide.

In the case of camphor some small pieces were fused so as to adhere to the sides of the tube near its upper end, and the tube was then filled with carbonic acid gas. The temperature being 12° C., the camphor began to melt when pressure was applied, and ran down the sides of the tube before the mercury appeared in sight. On suddenly releasing the pressure when the tube was full of liquid at 50° C., the sides of the tube became coated with crystals of camphor, and these rapidly dissolved again when the pressure was increased.

Other substances were investigated with similar results, and in the opinion of Professor Dewar, the carbonic acid behaves throughout as if it formed an unstable compound with the other substance present, and this compound is decomposed and reconstituted according to the conditions of temperature and pressure.

216. Liquid and Vapour Densities up to the Critical Point.— When a vapour is compressed to liquefaction in a tube, a means of determining the density of both the liquid and saturated vapour is afforded. By this method the saturated vapour density and other physical constants of hydrochloric acid were deduced by Mr. G. Ansdell.[1] A tube, such as that used by Andrews, was filled with the gaseous substance, and its mass became known by observation of the initial volume, pressure, and temperature. The pressure was then increased till the condensing point was reached, and the volume was then noted. This volume gives the density of the saturated vapour, and may be determined by taking the mean of two observations— one at the point where the volume diminishes, and the manometer ceases to show increase of pressure, and the other in the reverse

[1] G. Ansdell, *Proc. Roy. Soc.*, vol. xxx. p. 117, 1879-80.

operation, when the volume is allowed to increase, and its value is observed at the point where the manometer shows a slight decrease of pressure.

The mercury was then caused to rise in the tube till the whole gas was liquefied. The liquid now filled the top of the tube and its volume was observed; the tube being already carefully calibrated. This volume gave the density of the liquid. From the results of the experiments it appears that the density of the saturated vapour steadily increases as the temperature rises up to the critical point, while that of the liquid diminishes, and near the critical point the two approximate to equality. In Fig. 112 the volume of the saturated vapour—that is, the whole volume occupied when the gas is just at the condensing point—is plotted for various temperatures along the curve AC, while the liquid volumes at the same temperatures are shown by the curve BC. A mutual union of the two curves is indicated at the critical point, but experiments could not be made nearer than 0°·25 C. to this point on account of the rapid change of volume. This equality of volume or density at the critical volume is what would be naturally expected, and it is in accordance with similar experiments by MM. Cailletet and Mathias.

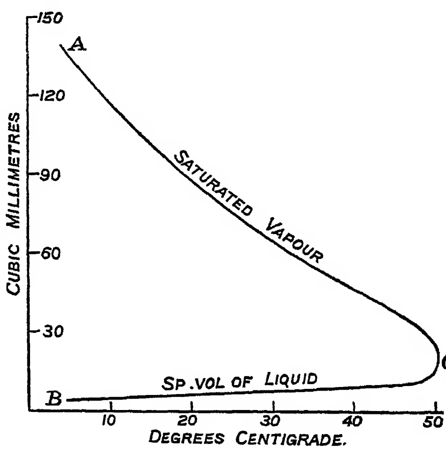


Fig. 112.

A number of experiments on ether led Avenarius[1] to the conclusion that the density of the saturated vapour is not the same as that of the liquid at the critical point. Mr. Ansdell, however, points out that as the critical temperature of ether is 192°·6 C., Avenarius was under the disadvantage of working at a high temperature, which it would be difficult to keep constant to within half a degree centigrade.

On the other hand, the critical temperature of hydrochloric acid is fairly low, and the temperature in Mr. Ansdell's experiments could be kept constant to within $\frac{1}{20}$ of a degree. The following table contains the results of the whole series of experiments on hydrochloric acid :—

[1] Avenarius, *Mém. Acad. Sci.*, St. Pétersbourg, 1876-77.

Temperature	Volume of Saturated Vapour.	Ratio of Volume of Vapour at 1 Atmo. to Volume at Condensing Point.	Volume of Liquid.	Ratio of Volume of Saturated Vapour to Volume of Liquid.	Pressure in Atmos.
4° C.	137·31	38·89	7·55	18·18	29·8
9·25	118·96	45·75	7·90	15·05	33·9
13·8	103·50	53·19	8·35	12·39	37·75
18·1	91·77	61·17	8·74	10·50	41·80
22·0	81·19	70·06	9·10	8·92	45·75
26·75	69·69	82·94	9·50	7·33	51·00
33·4	55·75	105·98	10·12	5·50	58·85
39·4	44·85	134·33	10·68	4·19	66·95
44·8	36·34	168·67	11·96	3·03	75·20
48·0	31·33	197·60	12·00	2·61	80·80
49·4	27·64	224·96	12·92	2·13	84·75
50·56	25·70		14·30	1·79	85·33
51·00	23·96		...		.

The compressibility at various temperatures was—

Temperature	47°·0	41°·6	33°·0	22°·7	15°·85	10°·5	5°·7
Compressibility	0·00166	0·00123	0·00096	0·000635	0·00062	0·00054	0·000397

and the density of the liquid was—

Temperature	0° C.	7°·5	11°·67	15°·85	22°·7	33°·0	41°·6	47°·8
Density . .	0·908	0·875	0·854	0·835	0·808	0·748	0·678	0·619

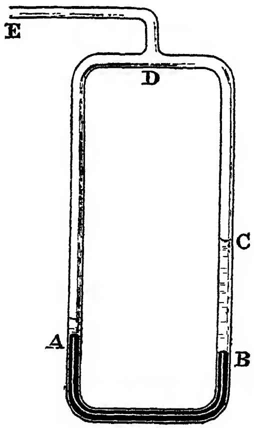


Fig. 113.

In the experiments of MM. Cailletet and Mathias[1] the method of determining the density of the liquid differed from that adopted by Ansdell. The mercury was not forced up till liquefaction was completed and the upper end of the tube filled with liquid alone, but the gas tube and compression pump were connected to a piece of apparatus like that shown in Fig. 113. This consists of a tube ABC, the two arms of which are united at D and communicate through the tube DE with the gas tube and compression pump. The lower part of the tube contains some mercury AB. On cooling the tube and gradually increasing the pressure liquefaction takes place in both arms. After a small

[1] Cailletet and Mathias, *Journal de Physique*, 2e, tom. v. p. 549, 1886.

quantity of liquid is thus obtained in each arm the condensation in A is stopped, and the arm BCD is alone cooled, and condensation is allowed to proceed in it till a column of liquid BC of a convenient height is obtained. The difference of level of the mercury in the two arms gives the weight of the column of liquid above B diminished by that above A. The object of having liquid in both arms is to correct for the difference of surface tension which would exist if the mercury at A were in contact with the gas, and that in B with the liquid.

By this means the density of the liquid is found, and the results of the experiments were found to be represented by the following formulæ:—

For nitrous oxide from $-20°{\cdot}6$ C. to $+24°$ C.—

$$\rho = 0{\cdot}342 + 0{\cdot}001666\theta + 0{\cdot}0922\sqrt{36{\cdot}4 - \theta}.$$

For carbonic acid between $-34°$ C. and $+22°$ C.—

$$\rho = 0{\cdot}350 + 0{\cdot}0035\theta + 0{\cdot}101\sqrt{31 - \theta},$$

and for ethylene at $-21°$ C., $-3°{\cdot}7$, $4°{\cdot}3$, and $6°{\cdot}2$ respectively, the density of the liquid was 0·414, 0·353, 0·332, and 0·31.

The saturated vapours were studied in a manner similar to that employed by Ansdell, namely, by noting the volume at the point of liquefaction. The formulæ obtained were:—

For nitrous oxide (saturated vapour)—

$$\rho = 0{\cdot}5099 - 0{\cdot}003610\theta - 0{\cdot}0714\sqrt{36{\cdot}4 - \theta}.$$

For ethylene—

$$\rho = 0{\cdot}1929 - 0{\cdot}00188\theta - 0{\cdot}0346\sqrt{9{\cdot}2 - \theta},$$

and for carbonic acid—

$$\rho = 0{\cdot}5668 - 0{\cdot}00426\theta - 0{\cdot}084\sqrt{31 - \theta}.$$

These formulæ belong to the general type

$$\rho = a + b\theta + c\sqrt{\theta_c - \theta},$$

where θ_c is the critical temperature, and if a curve be constructed with ρ and θ as co-ordinates it will be an arc of a parabola. Such a formula, of course, cannot be expected to be more than roughly approximate.

Quite recently M. Amagat[1] has employed a somewhat different method. In the method employed by Ansdell the saturated vapour density is estimated by observing the volume occupied by the substance in a graduated tube when the pressure is increased just to the point of liquefaction. It is, however, very difficult to determine the

[1] M. E. Amagat, *Comptes Rendus*, tom. cxiv. p. 1093, May 1892.

exact point at which the first traces of liquid appear, or at which the last traces disappear, and a small trace of air retards the liquefaction considerably, and then it takes place at a pressure notably superior to the maximum pressure of the pure vapour. It is only when some of the substance has been condensed that liquefaction takes place at the normal pressure. For this reason M. Amagat adopted the following method. The gaseous substance was compressed till part of it, say $\frac{1}{10}$ the total mass, was liquefied. When equilibrium was thoroughly established the volumes of the liquid and vapour were observed. The condensation was then proceeded with till $\frac{2}{10}$ or $\frac{3}{10}$ were liquefied and the new volumes were observed. If Δv and $\Delta v'$ denote the increase of liquid and the decrease of vapour when we pass from the first stage to the second, ρ and ρ' the densities of the liquid and saturated vapour respectively, then the mass of vapour condensed is

$$\rho'\Delta v' \text{ or } \rho\Delta v;$$

hence

$$\frac{\Delta v}{\Delta v'}=\frac{\rho'}{\rho}.$$

But if v and v' denote the total volumes of liquid and vapour, we have

$$\rho v+\rho' v'=m,$$

where m is the whole mass of the substance. From these two equations we obtain the quantities ρ and ρ' at once.

In this method the effect of the variation of the meniscus with temperature is eliminated, as it has no influence on the ratio of Δv to $\Delta v'$. The difficulty of the observations, however, increases rapidly as the critical point is approached, the instability of the substance rendering it difficult to obtain the meniscus in a steady position.

While carrying out these experiments M. Amagat noticed some interesting effects which had not been previously recorded. Thus by slow compression the meniscus disappeared at a temperature inferior to that of the critical point (at 30°·5 C., for example, in the case of carbonic acid). As long as the meniscus existed the interior generators of the tube appeared broken at its level (on account of the difference of refractive index) in such a way as to produce the appearance of a sudden diminution of internal diameter of the tube. At the moment of vanishing of the meniscus the breach in the generators disappeared and was replaced by two curves joining very regularly the two portions of each generator, the density at the same time appearing to pass in a continuous manner through all values from ρ to ρ'. This appearance was very transitory. An opaque horizontal band, resembling a thick emulsion, suddenly sprang up towards the middle of the

curvature and then disappeared. The meniscus then vanished with the broken generators, and a shower of fine drops fell upon the surface of the liquid and agitated it violently. In some cases the rain of droplets resembled the bubbles of vapour rising in a boiling liquid, and sometimes bubbles rose while the droplets fell, both phenomena occurring simultaneously.

These facts show how difficult it is to make measurements at within two or three tenths of a degree of the critical point. M. Amagat was, however, able to obtain good results by this method up to 31° C. with carbonic acid. The results of his experiments are shown

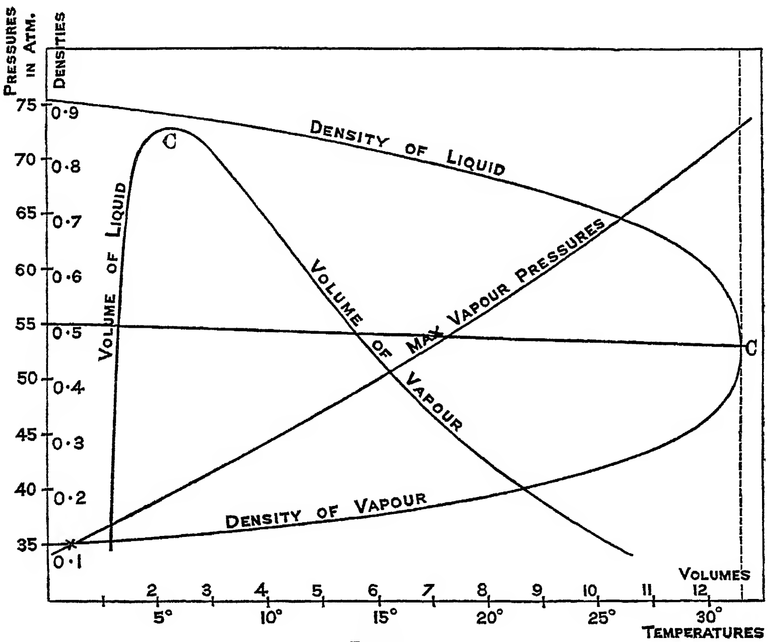


Fig. 114.

in Fig. 114, where the saturated vapour and liquid densities are represented by a curve having the densities for ordinates, and the corresponding temperatures for abscissæ. This curve, like those of MM. Cailletet and Mathias, resembles a parabola having its axis somewhat inclined to the axis of temperature. The locus of the middle points of its chords is accurately a right line, but the summit of the curve is much flatter than that of a true parabola, the densities of the liquid and vapour rapidly approaching equality at the critical temperature. At this temperature the two branches of the curve unite.

On the same diagram is represented the curve of vapour pressure

having the same temperatures for abscissæ, and the corresponding pressures as ordinates. The intersection of this curve with the ordinate at the critical temperature gives the critical pressure. All the critical constants are thus determined. For carbonic acid M. Amagat finds

$$\theta_c = 31^\circ{\cdot}35 \text{ C.}, \; p_c = 72{\cdot}9 \text{ atm.}, \; \rho_c = 0{\cdot}464.$$

The remaining curve shows the water-line and steam-line—that is, the border curve or locus of points at which the substance is all liquid or all saturated vapour. The pressures being ordinates and the volumes abscissæ, it gives the volume of the substance when it is all saturated vapour or all liquid at any temperature up to the critical point. It is thus an inverse of the parabolic curve, which gives the corresponding densities. The results of the experiments on carbonic acid are contained in the following table :—

Temp.	Liquid Density. ρ.	Vapour Density. ρ'.	Max. Vapour Pressure Atm.	Temp	Liquid Density. ρ.	Vapour Density. ρ'.	Max. Vapour Pressure Atm.
0°	0·914	0·096	34·3	18°	0·786	0·176	53·8
1	0·910	0·099	35·2	19	0·776	0·183	55·0
2	0·906	0·103	36·1	20	0·766	0·190	56·3
3	0·900	0·106	37·0	21	0·755	0·199	57·6
4	0·894	0·110	38·0	22	0·743	0·208	59·0
5	0·888	0·114	39·0	23	0·731	0·217	60·4
6	0·882	0·117	40·0	24	0·717	0·228	61·8
7	0·876	0·121	41·0	25	0·703	0·240	63·3
8	0·869	0·125	42·0	26	0·688	0·252	64·7
9	0·863	0·129	43·1	27	0·671	0·266	66·2
10	0·856	0·133	44·2	28	0·653	0·282	67·7
11	0·848	0·137	45·3	29	0·630	0·303	69·2
12	0·841	0·142	46·4	30	0·598	0·334	70·7
13	0·831	0·147	47·5	30·5	0·574	0·356	71·5
14	0·822	0·152	48·7	31·0	0·536	0·392	72·3
15	0·814	0·158	50·0	31·25	0·497	0·422	72·8
16	0·804	0·164	51·2	31·35	0·464	0·464	72·9
17	0·769	0·170	52·4	..	...		.

217. James Thomson's Hypothesis.—Two years after the publication of Andrews's experiments on the isothermals of carbonic acid, Professor James Thomson[1] supplemented these curves by an ingenious speculation suggested by the shape of the isothermals immediately above the critical temperature, as well as by the idea of continuity of transformation so much insisted on by Andrews. Thus in Fig. 115 the broken line ABCDE represents the ordinary isothermal of a substance passing from the liquid to the gaseous state. The part AB refers to the liquid state, and is approximately a straight line parallel to the axis of pressure. At

[1] J. Thomson, *Proc. Roy. Soc.*, 1871.

B the vapour pressure is equal to the external pressure, and the substance begins to separate into a mixture of saturated vapour and liquid. The quantity of vapour increases at the expense of the liquid till D is reached, and here the substance is all converted into saturated vapour. While this transformation is in progress the pressure remains constant, and the line BD, representing the isothermal of the mixture, is parallel to the axis of volume. Beyond D the substance is a non-saturated vapour, and the isothermal approximates more and more closely to that of a perfect gas. In the whole isothermal there are breaches of continuity

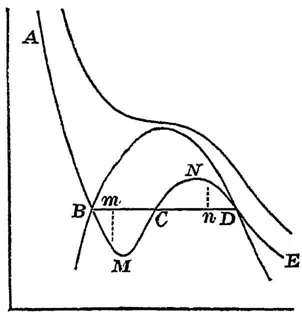


Fig. 115.

at B and D, if the temperature is below that of the critical point, but no such discontinuity appears in the case of an isothermal above the critical temperature. Here the curvature of the isothermal undergoes no sudden change at any point. The whole curve is continuous and unbroken throughout its course. The same remarks apply to the state of the substance. Along the line AB the whole mass is liquid and homogeneous throughout. At B discontinuity of state sets in, one portion being liquid and the other portion vapour. At D the simultaneous existence of the two states ceases, and the whole mass again assumes a uniformity of state.

In order to complete the continuity which exists above the critical temperature, and extend it to transformations below that temperature, Thomson put forward the suggestion that AB and DE are portions of the same continuous curve, and are joined by some ideal branch, such as BMCND, along which the substance might pass continuously from the liquid to the gaseous condition without any separation into two distinct states simultaneously existing in contact with each other. This part of the curve is very interesting, for along the portion BM the condition of superheated liquids, as exemplified in the experiment of Donny and Dufour (Art. 168), finds representation, and along the portion DN the condition of supersaturated vapours finds place. Thus the abnormal conditions of both liquids and vapours are embraced by Thomson's curve, and the so-called *difficulty* of commencement of change of state is merely the passage of the substance along the curve BMCND for some distance beyond B or D.

The condition of the substance at any point along this curve is one of uniformity throughout the mass, but it is essentially one of unstable equilibrium for any considerable displacement. Thus the vapour

at N is what we have termed supersaturated, and if the equilibrium be disturbed, condensation will set in, and the point representing the state of the substance will fall with a sudden decrease of volume to n, where the mass is partly liquid and partly vapour. In the same manner at M the condition is that of a uniform superheated liquid, and if the equilibrium be disturbed a sudden formation of vapour with explosive violence takes place, and the condition of stable equilibrium is assumed at m, where the substance is partly liquid and partly vapour.

Along the portion between M and N the curve slopes upwards, indicating that the volume and pressure increase simultaneously, an unstable condition which is not easily conceived, and which can never be realised in a homogeneous mass. Experimental evidence of this part of the curve cannot therefore be expected, unless perhaps, as J. Thomson himself suggested, it may exist in passing through the thin surface film of a liquid in contact with its own vapour.

If the isothermal curves for any substance be traced, each on a separate sheet of cardboard, the upper portion of the cards being cut away along the curves, and if these cards be placed with their planes parallel and at distances equal to the corresponding difference of temperature, they will form the characteristic surface of the substance, and exhibit the relation between p, v, and θ. Thomson constructed such a model for carbonic acid from the curves of Fig. 115. This surface exhibits very clearly the remarkable changes of volume at and near the critical point, and it assists in giving a clear view of the nature and meaning of the continuity of the liquid and gaseous states.

The p, v, θ model.

Although the whole mass of a substance passing from the state of vapour at D to the liquid state at B cannot be made to pass continuously along the curved path DNCMA, yet during the process of liquefaction states corresponding to various points on this line may exist, and the passage under constant pressure for vapour to liquid along the straight line DBC may be the result of the passage of small portions of the substance, variously located throughout the mass, through the states represented by some such curve as that suggested by James Thomson. Thus, although the transformation as a whole appears discontinuous, the continuity may be present in various parts of the mass while the transformation is being conducted.

The question now arises as to how the line BD is situated with respect to the hypothetical curve BMND; in other words, being given the curve find the position of the line, or the pressure of normal ebullition at the temperature of this isothermal. The answer to the question appears to be that the right line must be drawn so that the

area BMC is equal to the area CND. The reasoning by which Maxwell[1] arrived at this conclusion is as follows. Suppose the substance to pass from B to D along the hypothetical curve in a state always homogeneous throughout, and to return to B from D along the straight line DB in the form of a mixture of liquid and vapour. Since the temperature is constant throughout, no work, on the whole, can have been converted into heat (Second Law, see p. 42). But the external work done in the first part of the process is represented by the area enclosed by the curve, and the ordinates at B and D with the axis of volume, while that done in the second is represented by the area enclosed by the line BD with the same ordinates and axis. Hence these areas must be equal and opposite; or, in other words, the area BMC is equal[2] to the area CND. The value of either area of course cannot be determined, and the shape of the curve between B and D cannot be determined until some general relation between the pressure volume and temperature has been established.

Passing along the right line BD, the substance is partly liquid and partly vapour, but in passing from the state of liquid, at B, to that of saturated vapour, at D, along the curve suggested by Thomson, the substance is at each point of the path homogeneous throughout. The equality of areas just mentioned may therefore be stated in either of the following ways: "The pressure of the saturated vapour is such that

[1] Maxwell, *Nature*, vol. xi., 1875.

[2] The equality of these areas has been deduced by Clausius (*Wied. Ann.*, vol. ix. p. 337, 1880) from the algebraic statement of the Second Law. Assuming the cycle composed of the curve BMND and the line DB to be reversible, we have for the whole cycle (see Art. 292)

$$\int \frac{dQ}{T} = 0;$$

but throughout the cycle the temperature is constant, therefore

$$\int dQ = 0,$$

or no heat is, on the whole, given to the substance or taken from it during the process, and consequently as before the areas are equal. Thus, Maxwell's proof rests ultimately on the same axiom as that of Clausius, viz. on the second law of thermodynamics. Both, however, apply principles derived from experience to a case which cannot be realised experimentally, namely, the passage through the states represented by the curve, and which consequently casts doubt on the legitimacy of the conclusions. A proof of the theorem can also be derived from the theorems of Gibbs on the thermodynamic surface (Gibbs on the Equilibrium of Heterogeneous Substances, Chap. VIII., Sec. VII.).

It may be remarked that the internal energy of the mixture of liquid and saturated vapour at the point C, where the James Thomson curve is cut by the right line BD (Fig. 115), is not the same as the internal energy of the mass at the same point when in the hypothetical homogeneous state, but the internal energies in the two states at C differ by the area of either loop BCM or CDN.

the external work done during vaporisation is the same as that which would be performed if the substance increased its volume by the same amount, while at each stage of the transformation it remained homogeneous throughout," or "the pressure of a saturated vapour is equal to the *mean pressure* of the substance while receiving an increase of volume corresponding to complete vaporisation, and remaining at each stage of the process homogeneous throughout."

A method of plotting the unrealisable, or James Thomson, part of the isothermal curve has been described by Professors Ramsay and Young.[1] The relation between temperature and pressure is determined by drawing vertical lines (constant volume) across the isothermal curves, cutting them in points which correspond to certain definite pressures, which may be determined from a properly constructed diagram. A series of equi-volume lines may thus be plotted out by using the temperatures as ordinates and the pressures as abscissæ. All such lines were found to be straight, the relation between pressure and temperature at constant volume being linear and of the form [2]

$$p = b\Theta - a,$$

where a and b are constants depending on the volume chosen, and varying with it. The values of a and b being found by experiment for any volume at temperatures above the critical point, extrapolation was then applied to temperatures below the critical point, and the relation between pressure and temperature determined along the unrealisable part of the curve. Experimentally the pressure may be cautiously reduced below the point at which boiling occurs, and similarly a part of the curve on the other side can be realised by having the vapour in a space free from dust, so that condensation does not begin, although the temperature is below that of condensation.

The equality of the areas of the curve above and below the horizontal vapour line, as already referred to, was tested and verified by tracing the curve in this manner on tin plates, and cutting out the segments and weighing.

NOTE.—Near the critical point small changes of pressure are attended by considerable changes of density. M. Gouy (*Comptes Rendus*, tom. cxv. p. 720, 1892) has consequently directed attention to the important influence of the weight of superincumbent mass of fluid on the lower strata of a substance near its critical point. The effect of this pressure will be to place the lower strata under pressures higher than that appertaining to the critical point while the upper strata are still at lower pressures. The upper and lower strata may thus be at very different mean densities, and in M. Gouy's opinion this may explain the observations of MM. Cailletet and Colardeau (see further a note by G. Zambiasi, *Phil. Mag.* vol. xxxvi. p. 230, Aug. 1893).

[1] *Nature*, vol. xliv. p. 276 and p. 608, 1891.

[2] The equation of Van der Waals is of this form (see p. 419).

SECTION VII

ON EQUATIONS RELATING TO THE FLUID STATE OF MATTER

218. Early Experiments on Boyle's Law.—A perfect gas has been referred to already as an ideal substance which rigorously obeys Boyle's law. The substances which are ordinarily termed gases and vapours obey this law only more or less approximately. Within fairly wide limits the volume of any ordinary gas varies very approximately in the inverse ratio of the pressure to which it is subject. This law was discovered by Robert Boyle in 1660, and in 1661 he presented to the Royal Society his work, "Touching the Spring of Air and its Effects." With respect to the experiments on air he says: "'Tis evident that as common air when reduced to half its natural extent obtained a spring about twice as forcible as it had before, so the air, being thus compressed, being further crowded into half this narrow space, obtained a spring as strong again as that it last had, and consequently four times as strong as that of common air."

According to the dynamical theory of gases Boyle's law is a consequence of the comparatively very wide separation of the molecules. When the molecules are widely separated, so that they possess free paths, during which they move in right lines, and are free from mutual influences, the time spent in mutual influence becomes vanishingly small compared with the time spent in traversing the free path, and as a consequence the mutual effect of the molecules on each other becomes negligible, at least in a first approximation. The nature of the molecules and their mutual actions when near each other are thus eliminated from consideration. Such perfect freedom of a system of molecules from mutual influence is only attainable ideally as a limiting case. In the gases found in nature the time spent by any molecule in its collisions with the others is not vanishingly small compared with the whole period, and for this reason the effect of the mutual interactions of the molecules becomes sensible, and deviations from the law of Boyle of greater or less magnitude are exhibited.

Boyle himself does not appear to have considered this law to possess the wide generality afterwards attributed to it. He believed that for pressures above four atmospheres the compression of air was less than the amount deduced from the law, and Muschenbroek[1] appears to have arrived at the same conclusion.

Sulzer and Robison[2] both obtained the opposite result, and found that when the pressure was increased in the ratio of 7 to 1, the density increased in the greater ratio of about 8 to 1. This indicated a very wide divergence from the law, and must be attributed to faulty apparatus and the mode of observation, for later experiments by Oersted and Swendsen,[3] with improved apparatus, gave results which were very consistent with the law, although, on the whole, the density appeared to increase somewhat faster than the pressure. This, however, they attributed to errors of observation.

The next series of experiments was by Despretz.[4] The direct object of this investigation was to determine if all gases were equally compressible. It consequently was not ascertained if any particular gas obeyed Boyle's law, but rather that the different gases were compressed by different amounts when subjected to the same increase of pressure; and hence, if any one of the gases examined obeyed the law accurately, the deviations of the others from it could be deduced. The method of experiment was to enclose different gases in barometer tubes standing in the same cistern. The tubes were all of the same length, and the quantity of gas in each was so adjusted that initially the mercury stood at the same level in all the tubes. The system was then placed in a tall cylinder filled with water and fitted with a screw, by which the pressure could be increased at pleasure. It was then found that when the pressure was increased the previous equality of volume of the various gases became destroyed, and that the level of the mercury stood higher in some of the tubes than in others. It was thus found that such gases as carbonic acid and ammonia were more compressible than air, and that when the pressure exceeded 15 atmos., hydrogen exhibited an opposite effect. Up to 15 atmos. no difference of behaviour between air and hydrogen could be detected, but at higher pressures the hydrogen possessed a sensibly greater volume. This showed that of all the gases examined hydrogen was the least compressed at high pressures, or that the product pv was greater for air than for any other gas except hydrogen. If the values

[1] See the introduction to Regnault's Memoir on the compressibility of gases (*Mém. de l'Acad.*, tom. xxi.).

[2] Robison, *Mechanical Philosophy*, vol. iii. p. 637.

[3] *Edin. Journal of Science*, vol. iv. 1826.

[4] Despretz, *Ann. de Chimie et de Physique*, 2e, tom. xxxiv. pp. 335, 443; 1827.

of pv were tabulated from such an experiment, while the temperature was maintained constant, the extent to which the various gases disobeyed Boyle's law would be placed in evidence, and if every precaution has been taken to obtain them perfectly free from aqueous vapour, and all other impurities, the discrepancies must be attributed to an actual difference of compressibility of the various gases.

The research was next taken up by Pouillet,[1] who followed the method of Oersted and Despretz. He compared the compressibility of two gases contained in tubes about 2 m. long, and he concluded that oxygen, hydrogen, and nitrogen were equally compressible up to 100 atmos., and that sulphurous acid, carbonic acid, ammonia, etc., were notably more compressed than the former under high pressures. It still remained, however, to test the obedience of any single gas to Boyle's law; it was still believed that air obeyed the law, and the investigation of this point was taken up by Dulong and Arago.[2] Their experiments ranged up to 27 atmos., and within these limits they found that the observed volume was always slightly less than that calculated by the law. From an inspection of the numbers furnished by their experiments it appears that the difference between the observed and calculated volumes did not increase but rather diminished as the pressure increased. The difference, however, was always very small, and fluctuated a good deal in magnitude, so that it could not be concluded with confidence that any deviation from Boyle's law had been proved. For this reason the whole matter was investigated by Regnault[3] in a much more comprehensive manner.

[1] Pouillet, *Éléments de Physique*, tom. i. p. 327.

[2] Dulong et Arago, *Ann. de Chimie et de Physique*, 2e, tom. xliii. p. 74, 1830.

[3] Regnault, *Mém. de l'Acad.*, tom. xxi. p. 329.

In Regnault's experiments on Boyle's law the divergence of pv could not have been due to errors of observation. The differences would have required an error of reading of the pressure of from 2 to 118 mm.

Regnault represented the results of his experiment by a formula—

$$\frac{p_0 v_0}{pv} = 1 \pm A\left(\frac{v_0}{v} - 1\right) \pm B\left(\frac{v_0}{v} - 1\right)^2.$$

In his second memoir he proposed the formula (p being expressed in metres of mercury)—

$$\frac{0{\cdot}76 v_0}{pv} = 1 \pm A(p - 0{\cdot}76) \pm B(p - 0{\cdot}76)^2.$$

For air and nitrogen A was negative and B positive; for carbonic acid both A and B were negative; and for hydrogen both were positive.—*Relation des Expériences*, tom. ii. p. 237, etc.

The formula—

$$pv = pR(a\Theta + b) + R\Theta,$$

connecting the pressure, volume, and temperature of a gas, was proposed by Schroder

The method of experiment adopted was to enclose the gas under examination in a glass tube of accurately determined capacity, and surrounded by a bath kept at a uniform temperature. The gas filled the tube initially, and its pressure p_0 was registered by means of an open air mercury manometer. The pressure was then increased by forcing the mercury to rise from a cistern below into the manometer tube, and this was continued till the volume of the gas was reduced to half its initial volume, or very approximately so. Thus if Boyle's law is obeyed, and if $v_0 = 2v$, then we should have $p = 2p_0$. In practice it was more convenient to bring the final volume v approximately to the value $\frac{1}{2}v_0$, and then observe the pressure p, when the initial pressure p_0 was varied by admitting different quantities of gas into the tube. The following table contains the results of Regnault's experiments on air, nitrogen, hydrogen, and carbonic acid. It will be observed that in no case was the product pv found to be constant, but that the quotient p_0v_0/pv exceeds unity

Air.		Nitrogen		Carbon dioxide.		Hydrogen.	
p_0.	p_0v_0/pv.	p_0	p_0v_0/pv.	p_0.	p_0v_0/pv.	p_0.	p_0v_0/pv.
mm.		mm.		mm.		mm.	
738·72	1·001414	753·46	1·000988	764·03	1·007597	...	..
2112·53	1·002765	4953·92	1·002952	3186·13	1·028698	2211·18	0·998584
4140·82	1·003253	8628·54	1·004768	4879·77	1·045625	5845·18	0·996121
9336·41	1·006366	10981·42	1·006456	9619·97	1·155865	9176·50	0·992933

in the case of all the gases except hydrogen, and notably in the case of carbonic acid. In the case of hydrogen, however, the quotient was less than unity, and the inference was that within the limits of these experiments the product pv diminishes as the pressure increases for all the gases examined except hydrogen. In the case of this gas the deviation is in the opposite direction, the product pv increases, and the compressibility is less than that deduced from Boyle's law. This apparently peculiar and unexpected behaviour drew from Regnault the ironical remark that hydrogen was a "gaz plus que parfait."

Later experiments have, however, shown that this property is not

van der Kolk. From this it would follow that Boyle's law would hold only at the temperature

$$\theta = -\frac{b}{a}.$$

From Regnault's experiments M. Reye calculated that this temperature for air is 79° C., for CO_2 156° C., and for hydrogen $-41°$.

characteristic of hydrogen, but is exhibited by all other gases under high pressures, provided they remain in the gaseous state under these pressures. The general law seems to be that the product pv at first diminishes as the pressure is increased, and after attaining a minimum value it begins to steadily increase with the pressure. The exact course of the variations of pv is, however, modified to a considerable extent by the temperature at which the experiments are made. This is placed in evidence by the following important investigations of M. Amagat:— General law.

219. Amagat's Experiments.—The experiments of Regnault proved conclusively that Boyle's law is not rigorously obeyed by any gas in nature, and that in the case of all the gases examined, except hydrogen, the product pv diminished. Within the limits of these experiments it appeared that pv continued to diminish as the pressure increased. That this diminution of pv does not go on indefinitely, but that after decreasing for some time a value of the pressure was ultimately reached beyond which the product pv increased, as in the case of hydrogen, was first discovered by Natterer while endeavouring to liquefy the so-called permanent gases—oxygen, hydrogen, and air. Although the ground thus broken by Natterer[1] was of the highest interest and importance, nearly twenty years elapsed before the subject was taken up and examined more thoroughly. This was done simultaneously by Cailletet and Amagat in 1870; and the experiments of the latter[2] especially have advanced the knowledge

[1] J. Natterer, *Wiener Ber.*, 1850, 1851, 1854; *Pogg. Ann.*, vol. lxii. p. 139; vol. xciv. p. 436.

[2] Amagat, *Ann. de Chimie et de Physique*, 4e, tom. xxix.; 5e, tom. xxiii. p. 353. *Comptes Rendus*, tom. lxxiii. p. 183; tom. lxxv. p. 479; tom. cxv. p. 638, etc., 1892.

Amagat (*Comptes Rendus*, tom. xcix. p. 1153) gives the following table for the product pv for nitrogen and air at the ordinary temperature of 16° C., by which the correct reading of an ordinary air manometer may be determined at ordinary temperatures:—

Pressure in Metres of Mercury.	Nitrogen. pv.	Air. pv	Pressure in Metres of Mercury.	Nitrogen. pv.	Air. pv.
0·76	1·0000	1·0000	45	0·9895	0·9815
20	0·9930	0·9901	50	0·9897	0·9808
25	0·9919	0·9876	55	0·9902	0·9804
30	0·9908	0·9855	60	0·9908	0·9803
35	0·9899	0·9832	65	0·9913	0·9807
40	0·9896	0·9824	...	...	...

The pressure was determined by a column of mercury in a tube attached to a tower 65 metres in height.

of the subject in a marked degree. The method of experiment consisted essentially in the comparison of two manometers — one containing nitrogen, and the other containing the gas under examination. The latter was placed in a bath, the temperature of which could be varied at pleasure, and also maintained uniform during a series of observations. A previous investigation of the compressibility of nitrogen, made with the greatest care (the pressure being directly determined by means of an open air manometer), furnished the means of determining the actual pressure by means of the nitrogen manometer. Thus in the present investigation the volume and temperature of the gas under examination were directly observed, and the pressure was

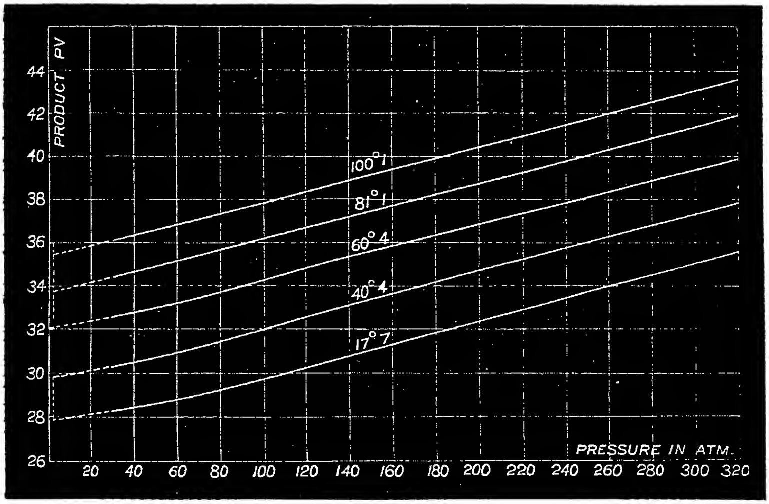


Fig. 116.—Hydrogen.

determined by the nitrogen manometer. All the quantities, p, v, and θ are thus known, and the variations of any function of these quantities may be determined. M. Amagat represented the variation of the product pv at constant temperature by tracing curves, of which the ordinates were the values of pv, and the abscissæ the corresponding values of p. An inspection of these curves shows that all the gases examined may be divided into two groups. Hydrogen is typical of the first group, and in this (Fig. 116) the curves are sensibly straight lines within the limits of the experiments. The lines corresponding to different temperatures are parallel to each other, but inclined to the axis of pressure in such a manner as to indicate that pv increases uniformly with the pressure. Carbonic

acid and ethylene are typical of the second group. In this case pv diminishes to a minimum, and then increases indefinitely with the pressure.

If Boyle's law were rigorously obeyed the curve connecting pv and p would be a right line, parallel to the axis of pressure, and the curve connecting p and v at constant temperature would be an equilateral hyperbola. Hence in the case of carbonic acid and other substances of this group, the curve connecting p and v is at first steeper than the hyperbola, and afterwards becomes less steep, and is not asymptotic to the axis of pressure.

The behaviour of nitrogen is shown in Fig. 117. At low pressures

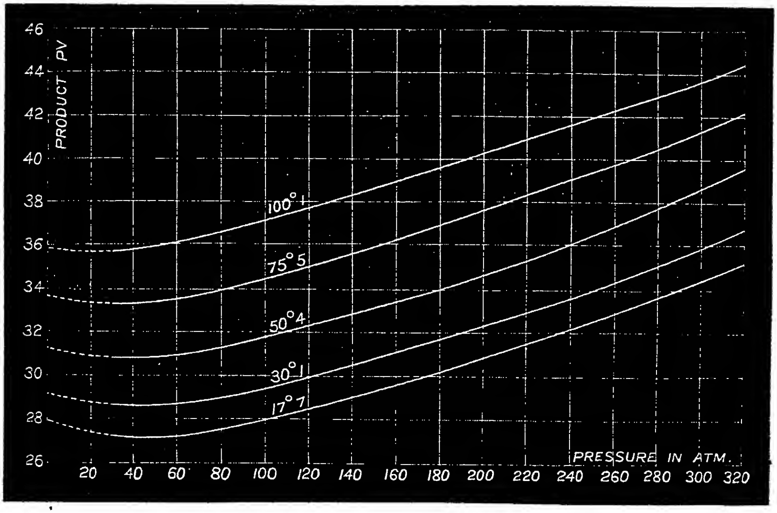


Fig. 117.—Nitrogen.

the product pv diminishes as the pressure increases, but after reaching a minimum the product begins to increase, and the curve rises like that of hydrogen. The figure shows the curves for experiments conducted at 17°·7, 30°·1, 50°·4, 75°·5, 100°·1.

The curves for ethylene are shown in Fig. 118. In this case the variation of pv is much more marked. The curve falls rapidly at first and is concave towards the axes. It then turns and rises almost uniformly. It will be observed that as the temperature increases the marked drop in the curve as well as the concavity disappears, and it is to be surmised that above a certain temperature the curve would, like that belonging to hydrogen, show only an upward slope. The fact that the product pv always increases for hydrogen is then a

sequence of the fact that at ordinary temperatures it is farther from its critical temperature than the other gases, or at least it is so far removed from it that the initial downward slope has disappeared from the curve. At low temperatures it is to be expected that the hydrogen

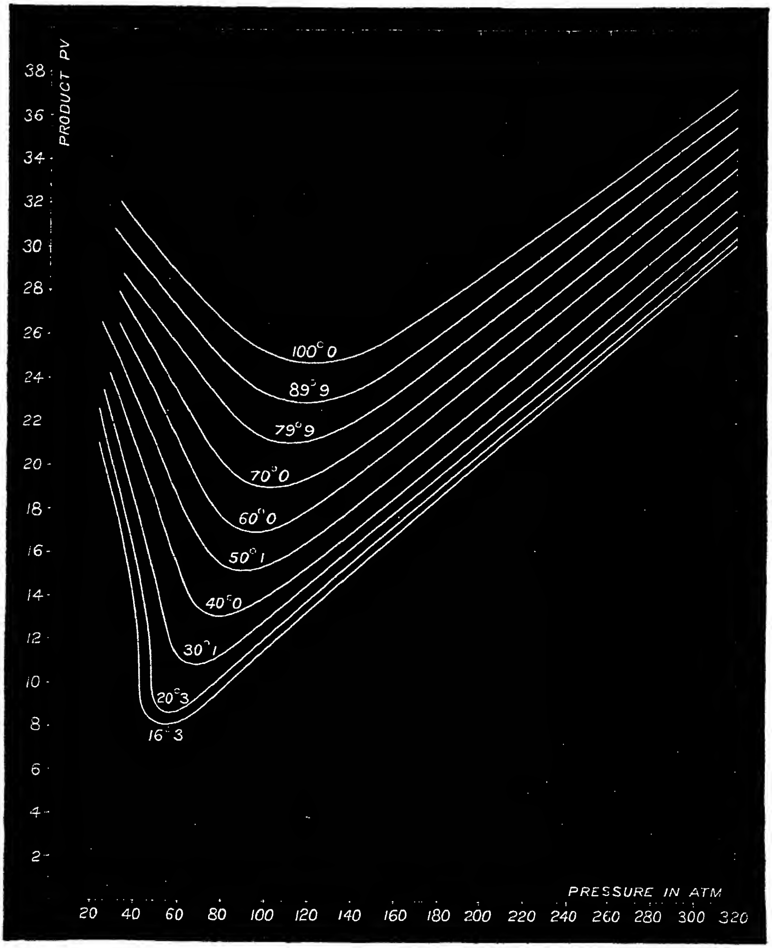


Fig. 118.—Ethylene.

curve would show a sag like that of nitrogen, and at very low temperatures like those of ethylene and carbon dioxide.

The curves for carbon dioxide are shown in Fig. 119, and resemble generally those of ethylene. Near the critical point the variation of the product pv is very rapid, but as the temperature becomes more

elevated constancy is more nearly approached, and the point of the curve where pv is least gradually recedes from the origin. Thus, for ethylene at 16°·3 C. the minimum value of pv corresponds to a pressure

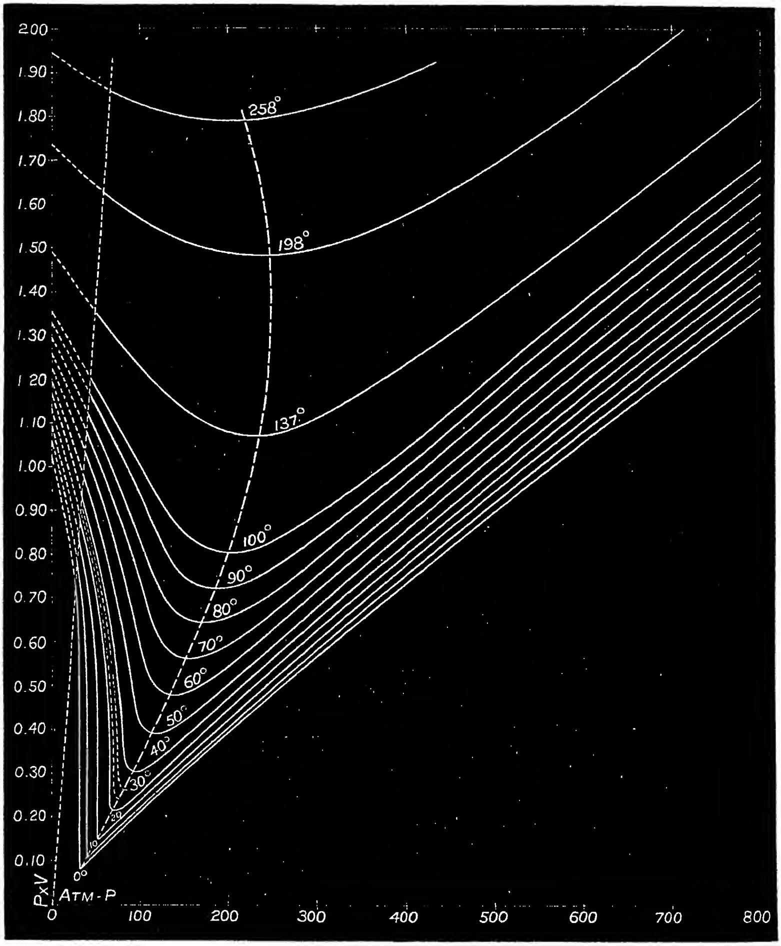


Fig. 119.—Carbon dioxide.

of 55 m. of mercury, while at 50° C. the corresponding pressure is 88 m., and at 100° it is 120 m. In the case of carbon dioxide the minimum values of pv at the temperatures recorded in Fig. 119 were found by M. Amagat[1] to occur at the following pressures :—

[1] Amagat *Comptes Rendus*, tom. cxiii. p. 450, 1891.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
° C.	Atm.	° C.	Atm.	° C.	Atm.	° C.	Atm.
0	35	30	76	60	143	100	211
10	45	40	101	70	162	137	247
20	57	50	124	80	179	198	255
..	...	..	..	90	196	258	218

It appears from Fig. 119 that these minimum points advance to the right as the temperature rises, but that this displacement ceases at high

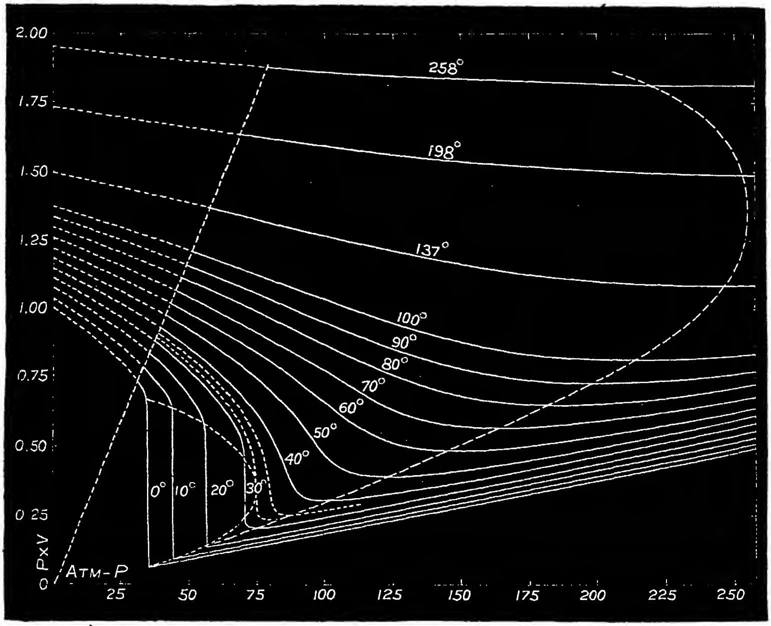


Fig. 120.—Carbon dioxide.

temperatures, and a retrograde motion sets in, so that the (dotted) curve passing through these points possesses a parabolic form. This is shown more clearly in Fig. 120, which exhibits the left-hand portion of Fig. 119 enlarged. The parabolic form of the dotted curve, passing through the minimum points, is here strongly brought out, as well as a second parabolic dotted curve, which appertains to temperatures below the critical point, and passes through those points at which condensation begins as well as those at which it is completed (cf. Fig.

114). The two dotted isothermals correspond to the temperatures 32° and 35° C.

For very high pressures the curves become for all substances a system of sensibly straight and parallel lines, and the equation of any one of these lines will obviously be

$$pv = ap + \beta,$$

or

$$p(v - a) = \beta.$$

The quantity a depends on the nature of the substance, while β depends on the temperature. When $v = a$ the pressure is infinite, and a is therefore the least volume into which the substance can be compressed. With this meaning then the above equation would be interpreted by saying that at high pressures the law of Boyle is obeyed by all substances at temperatures above the critical point, if we take as the volume of the gas the whole space in which it is enclosed, diminished by the least volume of the substance—that is, if the volume of the gas be considered as the space $v - a$ rather than the whole space v in which it is enclosed.

For the ratio a/v under a pressure of 760 mm. M. Amagat finds—

	Hydrogen.	Carbonic acid.	Ethylene.
$\frac{a}{v}=$	0·00078	0·00170	0·00231.

Difficulties at low pressures.

In all such experimental investigations the gas is compressed in a tube over mercury, and in testing the truth of Boyle's law a correction for the pressure of the mercury vapour must be applied. This correction has an insignificant effect at high pressures, but at low pressures it leads to great trouble and doubt. For this reason a new series of experiments was undertaken by Amagat[1] on the compressibility of air, hydrogen, and carbonic acid in a rarefied condition. The same question had been previously treated by Mendeleeff,[2] Kirpitschoff, and Hemilian, by Siljerström[3] and Amagat.[4] The results of these investigations differ considerably, and are attended by certain unavoidable sources of error which become more and more accentuated as the pressure is diminished. At low pressures the deviation from Boyle's law is exceedingly small, and at very feeble pressures it becomes so shrouded by the errors of experiment that it is impossible to be

[1] Amagat, *Ann. de Chimie et de Physique*, 5e, tom. xxii. p. 397, 1881; and tom. xxviii., 1883.

[2] Mendeleeff and Kirpitschoff, *Ann. de Chimie et de Physique*, 5e, tom. ii. p. 427, 1874; and tom. ix., 1876.

[3] P. A. Siljerstrom, *Pogg. Ann.* vol. cli. p. 451, 1874.

[4] Amagat, *Ann. de Chimie et de Physique*, 5e, tom. viii. 1876.

certain either of its magnitude or the direction in which it takes place. The method of experiment adopted by Amagat consisted in allowing the gas, enclosed in a glass cylinder of volume v and pressure p, to expand into another glass cylinder of sensibly equal volume v'. Both the cylinders were immersed in an oil bath kept at a constant temperature. After expansion the new volume of the gas was $v+v'$, and its pressure p' was measured. The quantities vp and $(v+v')p'$ could thus be compared, and the deviations from Boyle's law, if any, were determined. In the case of air no sensible deviation was found at low pressures, but carbonic acid yielded a product pv which diminished continuously as the pressure increased. This method of experiment, though apparently very simple, presents considerable experimental difficulties, and condensation of the gas on the walls of the enclosing vessel seems to be unavoidable.

Numerous experiments on the compressibility of nitrogen, sulphurous acid, carbonic acid, ethylene, and ammonia have been conducted by F. Roth,[1] the temperatures being carried to 180° C. by aniline vapour, and the pressures ranging up to 168 atmos. The apparatus employed was a modification of that adopted by Pouillet.

220. Compressibility of Gases under High Pressures. — The compressibility of gases under very high pressures has also been investigated by M. Amagat.[2] The method employed was that used for studying the compressibility of liquids[3] within the same limits of pressure, but the difficulty was far greater, arising chiefly from the smallness of the volume which a gas occupies when it is highly compressed. After numerous trials perfectly regular and concordant results were obtained by using for gauging the platinum wire tubes the method of reading by electrical contacts, which then served to estimate in the same tubes the volumes successively occupied by the compressed gas.

For the same reduction of volume Amagat found far higher pressures than those obtained by Natterer. This difference can be easily accounted for by the inevitable errors inherent in the method pursued by the latter. The following results refer to high pressures. For pressures below 1000 atmos. it was proposed to employ an apparatus which would enable the temperature to be raised far higher than it previously had been with these very high pressures, where it was only possible to work between 0° and 50°. The table gives, for the pressures specified in the first column, the volumes occupied at 15°

[1] Roth, *Wied. Ann.*, vol. ix., 1880.
[2] Amagat, *Comptes Rendus*, tom. cvii. p. 523, 1888.
[3] *Ibid.*, tom. cxv. p. 638, etc., 1892-93.

by a mass of the gas which occupied unit volume at 15° and 760 mm.

Atmos.	Air.	Nitrogen.	Oxygen.	Hydrogen.
750	0·002200	0·002262	...	..
1000	0·001974	0·002032	0·001735	0·001688
1500	0·001709	0·001763	0·001492	0·001344
2000	0·001566	0·001613	0·001373	0·001161
2500	0·001469	0·001515	0·001294	0·001047
3000	0·001401	0·001446	0·001235	0·000964

It is interesting to compare the compressibility of strongly compressed gases with that of liquids. In order to facilitate this comparison the following table from 750 atmos. to 3000 atmos. contains their coefficients of compressibility as usually defined, viz. dv/vdp:—

Limits of Pressure.	Air.	Nitrogen.	Oxygen.	Hydrogen.
Between 750 and 1000 atmos.	0·000411	0·000407	.	...
,, 1000 ,, 1500 ,,	0·000268	0·000265	0·000258	0·000408
,, 1500 ,, 2000 ,,	0·000167	0·000170	0·000160	0·000272
,, 2000 ,, 2500 ,,	0·000123	0·000122	0·000115	0·000197
,, 2500 ,, 3000 ,,	0·000093	0·000091	0·000091	0·000158

It is thus seen that at high pressures the three first gases have pretty much the same compressibility, and that it is of the same order as that of liquids. In fact, at 3000 atmos. it is virtually equal to that of alcohol at normal pressure. Hydrogen, however, has a much larger (almost double) compressibility at 3000, and it is almost equal to that of ether about the normal pressure. These compressibilities, like those of liquids, increase with the temperature, as is shown in the following table for hydrogen :—

Limits of Pressure in Atmos.	At 0°.	At 15°·4.	At 47°·3.
Between 1000 and 1500	...	0·000408	0·000416
,, 1500 ,, 2000	0·000263	0·000272	0·000280
,, 2000 ,, 2500	0·000196	0·000197	0·000208
,, 2500 ,, 3000	0·000156	0·000158	0·000158

The apparent densities are easily deduced from the apparent volumes given in the foregoing table, and if we assume the ordinary value of

the compressibility of glass, the following results are obtained for the real densities at 3000 atmospheres :—

Densities at 3000 Atmos. compared with Water.

Oxygen	1·0972 (apparent)	1·1054 (real)
Air	0·8752 ,,	0·8817 ,,
Nitrogen . . .	0·8231 ,,	0·8293 .
Hydrogen . . .	0·0880 ,,	0·0887 ,

The curves obtained by measuring p along the axis of abscissæ and pv along the ordinates are nearly straight lines, but all present a slight concavity towards the axis of abscissæ.

221. The Properties of Vapours. — At a time when it was supposed that the permanent gases rigorously, or with an extreme degree of proximity, obeyed Boyle's law, it had been found that vapours near their condensing points deviated considerably from the law. The experiments of Cagniard de La Tour (1822), Cahours[1] (1845), and Bineau[2] (1846), proved that as the pressure of an unsaturated vapour was increased the product pv diminished up to the condensing point, or that the coefficient of expansion of a vapour decreases from the condensing point, ultimately falling to that of a perfect gas as the temperature of the unsaturated vapour is raised. In the experiments of M. Cahours the coefficient of expansion appeared at first to increase to a maximum, and then to decrease gradually to that of a perfect gas as the vapour was gradually heated from the point of saturation. This peculiarity was explained on the supposition that at the saturation point condensation occurred on the walls of the enclosing vessel, and that as the vapour was heated this condensed layer evaporated and led to an abnormally high coefficient of expansion. According to Regnault's[3] experiments it appears that unsaturated water vapour may be regarded as practically obeying Boyle's law until the pressure reaches $\frac{4}{5}$ of the maximum vapour pressure.

The specific volumes of vapours, or their vapour densities at the point of saturation, are of great importance, as this quantity enters into many thermodynamic equations. The first experiments which established the influence of temperature and pressure on the densities of vapours were those of Fairbairn and Tate in 1860. These experiments (as well as those of Hirn[4] and Wüllner[5]) proved that the density of a saturated vapour is always greater than the value deduced on the

[1] Aug. Cahours, *Comptes Rendus*, tom. xx. p. 51, 1845; and tom. xxi. p. 625.

[2] Bineau, *Ann. de Chimie et de Physique*, 3e, tom. xviii. p. 226, 1846.

[3] Regnault, *Mém. de l'Acad.*, tom. xxvi. p. 200.

[4] Hirn, *Théorie Mécanique de la Chaleur.*

[5] Wullner, *Lehrb. d. Exp. Phys.*, vol. iii. p. 664.

supposition that Boyle's law is obeyed up to the point of saturation. Their method also admitted of the investigation of the behaviour of non-saturated vapours, for by superheating the enclosed vapour the difference of level of the mercury surfaces and the volume of the enclosed vapour could be observed, and in this method the errors arising in the estimation of the volume are not greater than those which ordinarily accompany the determination of the temperature, and the method is consequently favourable to the correct calculation of the specific volume of the saturated vapour.

An elaborate series of investigations on the compressibility of vapours and variations of the product pv near the condensing point was executed by Herwig[1] in 1868, but the method was not good for the determination of the specific volume of the saturated vapour. The vapour under examination was enclosed in one arm of a graduated glass tube in which the volume could be read off. The other arm of the tube communicated with a manometer which registered the pressure, and also with an air pump by means of which the pressure could be varied at pleasure. The vapour tube was immersed in a bath so that the temperature could be varied at pleasure, and the behaviour of the saturated vapour studied at various temperatures and pressures. The saturation point was determined by observing when the pressure commenced to diminish as the volume was gradually increased, and the sensitiveness of the method depends on whether an appreciable change of pressure is caused by a small change of volume at this point. This, however, is not the case, for the value of v corresponding to the exact point of saturation is very ill defined, the rectilinear part of the isothermal merging gradually into the hyperbolic, and large changes of volume giving rise to small changes of pressure.

This series of experiments led Herwig to the conclusion that the product pv for a vapour gradually diminishes as the pressure is increased up to the condensing point, and that if p_s, v_s, denote the pressure and volume of the substance at the condensing point, while p and v denote its pressure and volume at the same temperature when very far removed from this point—that is, in the state of a perfect gas—then the experiments might be represented by the formula—

$$\frac{pv}{p_s v_s} = \mathrm{C}\sqrt{\theta} = 0{\cdot}0595\sqrt{\theta},$$

the constant C being the same for all the substances examined. From this it follows that

$$p_s v_s = \frac{pv}{\mathrm{C}\sqrt{\theta}} = k\sqrt{\theta},$$

[1] Herwig, *Pogg. Ann.*, vol. cxxxvii., 1869 ; vol. cxli., 1870.

where k is another constant, which will be different for different substances.

This formula, if true, informs us that the product pv for a saturated vapour varies as the square root of the absolute temperature, and therefore enables us to calculate the specific volume of the saturated vapour at all temperatures from a table of vapour tensions. It also leads to the conclusion that at the temperature

$$\Theta = 1/C^2 = 282^\circ{\cdot}58 = 9^\circ{\cdot}59 \text{ centigrade}$$

the product $p_s v_s$ is the same as the constant value of pv under Boyle's law. This consequence of the formula has not been justified by experiment, and as Herwig did not extend his experiments through a sufficiently wide range of temperature, his formula cannot be regarded as possessing more than a very limited range of application.

Subsequently many of the results obtained by Herwig were verified by Wüllner and Grotrian,[1] but they found from a study of the same vapours that the quantity C in Herwig's formula could not be regarded as constant.[2] The method of experiment was a combination of that of Herwig with that of Fairbairn and Tate. The space in which the vapour was produced and studied consisted of three flasks of which the necks were downwards, and were graduated into parts of equal volume and communicated with a receiver full of mercury under a constant pressure. A fourth flask, placed in the same conditions, contained vapour always saturated in presence of an excess of liquid, which played the part of the outside vessel in the experiment of Fairbairn and Tate. The four flasks were placed in the same bath, and the volumes of the first three were in the ratio 1 : 2 : 4, and the weights of liquid placed in them were in the same ratio, so that they were all just saturated at the same instant. The temperature was raised till the three were filled with a dry vapour, and the pressure was then increased very slowly till mist appeared in them or on their walls. This was taken as the point of saturation. The observations made on the three flasks always agreed, but the pressure at which the mist appeared in them was always a little less than the maximum pressure of the saturated vapour in the fourth vessel.

This indicates, as M. Perot[3] remarks, that the curvature of the

[1] *Wied. Ann.*, vol. xi. p. 545, 1880.

[2] M. Perot (*Ann. de Chimie et de Physique*, 6e, tom. xiii. p. 145, 1888) finds that in the case of water the C in Herwig's formula remains sensibly constant and equal to 0·0526 within the limits of the experiments (68°·2 C. to 110°·5 C.). In the case of ether, however, it increased from 0·0428 at 30° C. to 0·0609 at 110°·5 C.

[3] M. Perot, *Ann. de Chimie et de Physique*, 6e, tom. xiii. p. 145, 1888.

isothermal is continuous at the point where the substance passes from the state of a vapour to that of a mixture of vapour and liquid; that it does not change suddenly from a hyperbola to a right line, but that condensation sets in at a pressure somewhat inferior to the maximum vapour pressure. This is shown in Fig. 121, where the isothermal is drawn with a rounded instead of a sharp corner at AB. Here condensation starts at A and the pressure gradually increases to its normal maximum value at B. It follows, therefore, that in the experiments of Wüllner and Grotrian the specific volume was measured at A, while in Herwig's and in those of Fairbairn and Tate it was estimated at the point B.

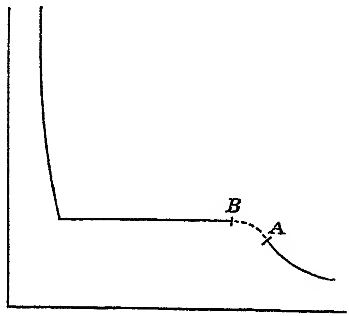


Fig. 121.

The same conclusions have been drawn by Battelli[1] from the results of some recent experiments. The vapour pressure was always found to augment somewhat during the initial stages of condensation, so that the corner of the isothermal was slightly rounded off as in the figures obtained by Andrews for carbonic acid containing a trace of air. This augmentation of vapour pressure was noticed by Regnault in the case of vapours formed in air or other gases, and was attributed by him to the adhesion of the vapour to the walls of the vessel, or the retardation of evaporation caused by the presence of the gas. Herwig observed the same effect when the vapour was unmixed with air or any other gas, and he attributed it to adhesion to the walls of the vessel. Wüllner and Grotrian proved the existence of this augmentation of pressure, as the volume decreased, in a decisive manner and under such conditions that it could scarcely be attributed to the walls of the vessel. In the experiments of Battelli the augmentation of pressure increased as the volume was diminished, even when the walls of the vessel were covered with a deposit of dew. This augmentation continues only up to a certain point where it ceases, and then the pressure remains constant while condensation progresses. In the opinion of Battelli it cannot be attributed to the presence of dissolved air, as precautions were taken to secure the purity of the liquid, and if it were due to the presence of air or a gas it should increase regularly as the volume is diminished. It consequently appears established that condensation commences some-

[1] Battelli, *Ann. de Chimie et de Physique*, 6e, tom. xxv. p. 38, 1892.

what before the maximum pressure is reached, and in Battelli's experiments it was found that the ratio of the pressure at the commencement of condensation to its maximum value was the same at all temperatures, but the ratio of the augmentation of pressure to the diminution of volume increased rapidly with the temperature. The coefficients of expansion under constant pressure increased more rapidly with diminution of temperature as the vapour approached saturation, and the rapidity of this increase was more sensible the higher the temperature.

The coefficient of increase of pressure at constant volume diminished progressively with the elevation of temperature, and these variations were more rapid the smaller the volume. With increase of volume the absolute values of these coefficients diminished.

Battelli also found that the quantity C in Herwig's formula could not be regarded as a constant; but that it is a function of the temperature, so that he proposes to replace the formula by the more general equation

$$\frac{pv}{p_s v_s} = \mathrm{A}\sqrt{\Theta}\left(a\Theta + \frac{b}{\Theta - \alpha}\right),$$

where A, a, b, α, are constants. This formula embraces the result obtained by Battelli that the product $p_s v_s$ increases as the temperature rises up to a certain value and then decreases.

The experimental investigation of the thermal properties of vapours has not yet, however, been sufficiently far advanced to establish the truth of any theoretic formula yet deduced. Grave discrepancies exist between the results of experiment and those deduced by theory, especially when the range of the experiments is large, and in most cases it is difficult to attribute the discrepancies to error of observation or fault of theory, for the results of different experimenters may differ considerably on account of the probable use of substances in different states of purity, and traces of impurities often modify the physical properties of a substance in a high degree.

222. Influence of Intermolecular Actions and the Magnitude of Molecules on the Characteristic Equation of the Fluid State.—It appears conclusively established by the foregoing investigations that no substance in nature accurately obeys Boyle's law, but that, as a general rule, the deviations from this law take place in such a manner that at first the augmentation of pressure with diminution of volume is not sufficiently great, and after a certain pressure is reached (which varies with the temperature) the opposite effect sets in, and there is a universal preponderance of increase of pressure. We shall now consider how these two opposite effects may be accounted for by

the dynamical theory when the size and mutual influence of the molecules are taken into account. In order that the simple equation $pv = R\Theta$ may be obeyed it is necessary (1) that the space actually filled by the molecules of the gas may be vanishingly small compared with the whole volume of the enclosure in which it is contained; (2) the time spent in a collision must be negligible compared with the average interval between two successive impacts; and (3) the influence of the molecular forces must be vanishingly small at the mean distance of the molecules. These conditions merely express the supposition that all intermolecular influence may be neglected. Conditions.

If these conditions are not fulfilled, deviations in various directions from the simple gaseous laws take place, which become more and more considerable as the molecular state of the gas corresponds less and less to these conditions. As the space occupied by a given mass of gas is diminished, the length of the mean free path becomes shorter, and the number of molecules in encounter at any instant bears a larger proportion to the number describing free paths. The exact nature of the effect of an encounter is unknown, but it is to be expected that when the number of encounters largely increases, the properties of the substance will be determined more by the nature of the mutual action between two molecules when in collision (*i.e.* within the sphere of each other's action) than by the motion of the molecules when describing their free paths, and for this reason deviations from the simple laws of gases may be anticipated. As the condensation increases the behaviour of the substance will become more complicated, and its state of aggregation may change, the mass passing partly or altogether into the liquid state, but the theoretical investigation of its general characteristics cannot be proceeded with until we know the nature of the action between molecules when they are so closely packed that each is constantly subject to the influence of the others. The experimental data for the study of this action are to be obtained from the study of the relations between density, pressure, and volume, such as that furnished by the work of Regnault, Andrews, Amagat, and Cailletet, and besides this in another direction by the study of the rate of diffusion and the viscosity of fluids.

Attempts have been made by several physicists[1] to deduce a

[1] Rankine (*Phil. Trans.*, 1854, p. 336) constructed the equation—

$$pv = R\Theta - \frac{C}{v\Theta},$$

in which R and C are constants. This equation closely resembles that derived by Joule and Thomson (*Phil. Trans.*, 1862, p. 579) from their experiments on the change

general equation connecting the pressure, volume, and temperature which will express the characteristic properties of any substance throughout the fluid state from the condition of a perfect gas to that of a liquid. In forming an equation which shall replace $pv = R\Theta$, the first consideration that presents itself is the manner in which the molecular attraction affects the pressure and volume of the mass. It is clear that the result of this attraction will be to increase the pressure inside the mass or produce what is termed a capillary pressure ϖ due to the surface layer, so that if the pressure on the walls of the enclosure is p, the pressure in the interior of the mass will be $p + \varpi$ where ϖ is some function to be determined.[1] In the second place, when the size of the molecules is taken into account the volume v becomes reduced by some quantity ϕ, and the first step is to replace the equation $pv = R\Theta$ by the more general equation—

$$(p+\varpi)(v-\phi)=R\Theta.$$

In this form the equation agrees with that constructed by Hirn[2] in which ϕ is the sum of the volumes of the molecules and ϖ the sum of the internal actions, or the internal pressure. In his further treat-

of temperature of a gas by expansion. Subsequently Recknagel (*Pogg. Ann. Ergbd.*, vol. v. p. 563, and vol. cxlv. p. 469, 1871-72) formed the equation—

$$pv=R\Theta\left(1-\frac{f(\Theta)}{v}\right),$$

which is the same in form as that of Rankine, the general function of Θ being placed in the final term instead of $1/\Theta^2$.

[1] The mutual attraction of the molecules diminishes the pressure on the walls of the enclosure, for each molecule in passing through the surface layer is acted on by an attractive force directed towards the interior of the mass by which its impact on the wall of the vessel is diminished. This capillary pressure seems to exist in steam in the form of clouds, and in tobacco smoke, as appears from the researches of Bosscha. In wet capillary tubes clouds show a meniscus like mercury, and are depressed in the same way. It probably rises into importance in the case of highly-compressed gases and vapours near the condensing point. The smaller the volume the larger this internal pressure becomes, so that it may ultimately equal or even exceed the pressure which the substance would exert on the walls of the vessel by the unobstructed motion of its molecules if molecular attraction did not exist; when this limit is reached no external pressure will be necessary to keep the substance within the enclosure; or, in other words, the gas has liquefied. Whether this occurs or not depends evidently on the magnitude of ϖ compared with the kinetic energy of the molecules, and if the latter is large—that is, if the temperature is high—no possible diminution of volume will render ϖ sufficiently great, and the gas cannot be liquefied. In other words, the critical temperature has been passed. A liquid might, therefore, be defined as a fluid substance in which the average kinetic energy of the molecules is unable to counterbalance the internal or capillary pressure caused by their mutual attraction.

[2] Hirn, *Théorie Mécanique de la Chaleur*, 3rd edit., tom. ii. p. 211.

ment of this equation, however, in which he seeks to determine the quantities ϖ and ϕ, he makes inferences which seem difficult to justify, and the results of which do not seem to agree with experiment.

The most celebrated equation of this kind was developed by J. D. van der Waals in 1879, and in it the effects of the size and the mutual attraction of the molecules are taken into account. This equation may be derived from the foregoing from the consideration that the attraction between any two elements of the mass is proportional to their product, and hence in a homogeneous fluid to the square of the density. At any given temperature, therefore, the capillary pressure ϖ will vary as the square of the density or inversely as the square of the volume. The quantity ϕ, on the other hand, is the value of the volume at any given temperature when the pressure is infinite, or the least volume into which it is possible to compress the fluid. This in the case of a system of particles in motion has been taken as four times the sum of the volumes of the particles.[1] Denoting this by b and the quantity ϖ by a/v^2, where a is for the present considered as a constant, we obtain the equation of Van der Waals—

$$\left(p+\frac{a}{v^2}\right)(v-b)=R\theta.$$

This equation gives isothermal curves agreeing closely with the earlier experiments of Andrews on carbonic acid, and exhibiting also the characteristic differences of form above and below the critical temperature. On comparison, however, with later experiments the equation has been found not to sufficiently represent the facts, and cannot be brought into accordance with them by altering the constants.

This arises from the limited considerations on which the term a/v^2 is introduced. The capillary pressure ϖ will obviously be influenced by other circumstances besides change of density. Van der Waals assumed it as self-evident that the mutual attraction of the molecules does not depend on the temperature, so that the quantity ϖ is a function of the volume only, and the molecular attraction remains unaltered when the substance is heated at constant volume. This might be true if the motion of a molecule at different temperatures differed only in the quantity of its mean kinetic energy but took place in all other respects in exactly the same way, the paths and the ratio

[1] The quantity b is called the co-volume, and is generally considered as proportional to the space u actually occupied by the molecules in a unit volume, so that $b=ku$ where k is the same for all gases. Van der Waals finds $k=4$ from considerations based on the theory of probability, while O. E. Mayer (*Kinetische Theorie der Gase*, p. 298) deduces the number $4\sqrt{2}$, and this latter number has been verified by E. Heilborn (*Phil. Mag.*, 5th, vol. xxxiv. p. 459, 1892).

of its velocities at different stages of the paths being exactly the same. In the case of a perfect gas it may be assumed that every pair of molecules separate immediately after collision, but when a gas is near its condensing point, it may happen that two molecules may not separate after collision, but that the molecules may collect in little groups and oscillate about each other. The number of such groups will increase as the temperature falls; and consequently, if this happens, the mean strength of the mutual attraction, or the pressure function ϖ, will increase as the temperature falls.

It would appear, therefore, that the quantity a in the formula of Van der Waals very probably varies with the temperature. In its present form no universal or rigorous validity can be ascribed to it, and although Van der Waals obtains it as the ultimate result of an elaborate and ingenious mathematical investigation, yet the assumptions introduced in the various stages of the work render the final equation little more than a first approximation to the truth. The essay of Van der Waals is, nevertheless, a bold and promising attack on an exceedingly difficult problem. He starts[1] with the theorem of Clausius that in stationary motion the mean kinetic energy of a system is equal to the mean virial, or (p. 96)

$$\tfrac{1}{2}\Sigma(mV^2)=\tfrac{3}{2}pv+\tfrac{1}{2}\Sigma\Sigma(Rr),$$

the final term representing the virial of the intermolecular forces. He then assumes that the temperature of a substance is measured by the mean kinetic energy of the molecules, but although this may be true for gases, it may not hold for liquids, or vapours near their condensing points, or for highly compressed gases. Assuming, however, for the present, that the mean kinetic energy is proportional to the temperature, the virial equation becomes

$$pv=R\Theta-\tfrac{1}{3}\Sigma\Sigma(Rr),$$

which shows the deviation from Boyle's law when the virial exists.

Experiment has proved that in gases the product pv diminishes at first, and after a certain stage increases, whereas in vapours pv diminishes up to the condensing point, and in the case of liquids p increases rapidly, while v remains nearly constant, so that pv increases rapidly. The diminution of pv points to an increasing positive virial, and hence to an attractive force R between the molecules. The increase of pv would, on the other hand, point to a negative virial and, at first sight, a

[1] *Die Continuität des Gasformingen und Flussigen Zustandes.* The Memoir of Van der Waals has been translated into English by Richard Threlfall and John F. Adair, *Physical Memoirs, Physical Society of London*, vol. i. part iii.

negative value of R, or an apparent repulsion between the molecules. Before a mutual repulsion between the molecules is assumed, it should be inquired if this apparent repulsion could be explained by the motion and mutual impacts of the molecules, just as the pressure of a gas on the walls of the enclosing vessel may be explained by the motion of the molecules without assuming the substance to be self-repellent. This apparent molecular repulsion at small volumes must be accounted for by the mutual impacts of the molecules, and in dealing with a system of moving molecules the complete characteristics of the substance cannot be deduced by considering the impacts on the walls of the enclosure alone. The term depending on the mutual collisions of the molecules must also be extracted from the virial,[1] but until the nature of a collision is fully understood the exact influence of this term cannot be ascertained. Van der Waals assumes the molecules to be elastic spheres which attract each other when not in contact, and he considers the effect of the size of the molecules in diminishing the length of the free path and finds this effect, in the case of a rare gas, to be the same as if the volume of the enclosure had been diminished by four times the sum of the volumes of the molecules. At a constant temperature the effect of the molecular attraction is to diminish the pressure on the walls of the enclosure by a quantity varying as the square of the density so long as the encounters take place, on the whole, between two molecules at a time and not between three or more.

The failure of the equation of Van der Waals to sufficiently represent the facts led Clausius[2] to construct an equation, which appeared to him to retain all that was correct in previous formulæ, and which also made allowance for the variation of molecular attraction with temperature. This equation gives the pressure in terms of the temperature and volume in the form

$$p=\frac{R\Theta}{v-\alpha}-\frac{c}{\Theta(v+\beta)^2},$$

where R, c, α, β are constants. This equation, like that of Van der Waals, gives a cubic for v for any given values of the temperature and pressure. As every cubic equation has either one or three real roots, both these equations furnish either one or three real values of v for any given condition of temperature and pressure. The one real

[1] In considering the effect of molecular attraction on the form of the virial, it appears that the difference of the average kinetic energies of a free and an entangled molecule is of special importance in the physical interpretation of the virial.

[2] Clausius, *Wied. Ann.*, vol. ix. p. 337, 1880; *Phil. Mag.*, June 1880.

root applies to the gaseous condition where a definite volume exists for every value of p and Θ. The three real roots apply to that region in which for given values of p and Θ the substance can exist either wholly as a saturated vapour, or altogether as a liquid, or as a mixture of the two. The latter volume does not exist as a definite volume, but the root corresponding to it is represented on the diagram (Fig. 122) by the point in which the rectilinear part of the isothermal, parallel to the horizontal axis, meets the curved or hypothetical part of the isothermal suggested by James Thomson.

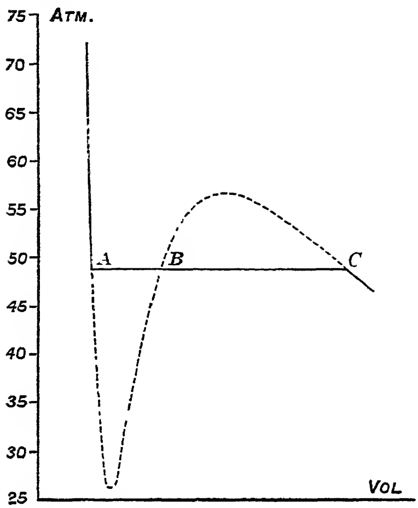


FIG. 122.—Curve for carbonic acid, after Clausius. Temperature 13°·1.

The equation of Clausius embraces four constants, to be determined by comparison with the results of four experiments on the values of p and v at four different temperatures. The equation of Van der Waals, on the other hand, embraces only three constants, which can be determined by three experiments. Hence, if both be regarded merely as empiric formulæ, a greater range and more general agreement with experiment would be expected from the equation of Clausius.

In the case of carbonic acid the values of the constants deduced by Clausius were, using the kilogramme and metre as units—

$$R=19{\cdot}273, \quad c=5533, \quad \alpha=0{\cdot}000426, \quad \beta=0{\cdot}000494.$$

The tables calculated by this formula show in general a satisfactory, and in some cases a strikingly good accordance with the results of experiment.

M. Sarrau[1] has further shown that the formula of Clausius represents the results of Amagat's experiments very satisfactorily in the case of hydrogen, nitrogen, and methane; but for carbonic acid and ethylene the range of accordance is much more limited.

From the consideration of the curves representing the results of his experiments M. Amagat[2] was led to replace the term a/v^2 in the

[1] Sarrau, *Comptes Rendus*, tom. xciv. pp. 639, 718, 845; 1882.
[2] Amagat, *Ann. de Chimie et de Physique*, 5e. tom. xxviii., 1883.

equation of Van der Waals by a general function of v, so that the equation takes the form

$$\left[p+\frac{a}{f(v)}\right](v-b)=R\Theta.$$

This contains the formula of Van der Waals as a particular case, but even in this more general form it fails to embrace the laws of compressibility of both the gaseous and liquid states throughout. In order to express the compressibility of a substance by a formula which will apply both to the liquid and gaseous states, recourse must be made to a more complicated type, such as

$$\left[p+\frac{a}{f(\Theta,v)}\right](v-b)=R\Theta,$$

which merely introduces the consideration that the internal pressure ϖ is a function of both volume and temperature. Of the foregoing, the formula of Clausius, which may be written in the form

$$\left[p+\frac{a}{\Theta(v+\beta)^2}\right](v-\alpha)=R\Theta,$$

is a particular case.[1]

This equation was constructed by Clausius[2] to represent the experiments of Andrews on carbonic acid, under the supposition that it would apply to other substances by changing the constants only. On trial, however, it was found that the equation, in this form, would not yield a satisfactory agreement with the results obtained from experiments on other substances; and in order to meet this deficiency, Clausius changed the quantity c/Θ in the final term of the equation (p. 421) into a general function of the temperature, and for this purpose he first wrote the equation in the form

$$\frac{p}{R\Theta}=\frac{1}{v-\alpha}-\frac{c}{R\Theta^2(v+\beta)^2},$$

[1] A general equation connecting the pressure, volume, and temperature has also been deduced by M. Aroldo Violi (*Rend. della R. Acc. dei Lincei*, vol. iv. p. 285; *Beiblatter der Physik*, vol. xiii. p. 66; and *Phil. Mag.*, June 1889) from the kinetic theory, on the basis of various hypotheses as to the mode of action of the molecules. The final equation is

$$\left[p+\frac{a}{2\{v(1-b)(1+\alpha\theta)\}^2}\right]v(1-b)=R,$$

where p is the pressure in metres of mercury, v the volume reduced to zero centigrade, θ the temperature centigrade, α the coefficient of expansion of a perfect gas, a the constant of molecular attraction, b the ratio of the volume of the molecules to the whole volume occupied by the substance.

[2] Clausius, *Wied. Ann.*, vol. xiv. p. 279, 1881; *Ann. de Chimie et de Physique*, 5e, tom. xxx. p. 433, 1883.

and then replaced $R\Theta^2/c$ by a general function Ψ of the temperature which vanishes with the temperature. The equation thus becomes

$$\frac{p}{R\Theta} = \frac{1}{v-a} - \frac{1}{\Psi(v+\beta)^2}.$$

This equation may of course be written in the form

$$\frac{p}{R\Theta} = \frac{1}{v-a} - \frac{27(a+\beta)}{8\Phi(v+\beta)^2}.$$

where Φ is a function of Θ which vanishes with Θ, and which, on account of the introduction of the factor

$$\frac{27}{8}(a+\beta),$$

is in addition equal to unity at the critical temperature (see p. 430).

223. Application of Clausius's Equation.—In order to apply this equation to the case of evaporation, let p denote the pressure of the saturated vapour, v_1 the specific volume of the liquid, and v_2 that of the saturated vapour. We have then the two equations—

$$\frac{p}{R\Theta} = \frac{1}{v_1-a} - \frac{27(a+\beta)}{8\Phi(v_1+\beta)^2} \quad . \quad . \quad . \quad \text{(liquid)} \quad (1)$$

$$\frac{p}{R\Theta} = \frac{1}{v_2-a} - \frac{27(a+\beta)}{8\Phi(v_2+\beta)^2} \quad . \quad . \quad . \quad \text{(vapour)} \quad (2)$$

A third equation is obtained by expressing that the work done in passing along the rectilinear part of the isothermal, which applies to the passage of the substance from being altogether liquid to being altogether saturated vapour, is the same as if the transformation took place along the theoretical curve joining the same two points and given by the above equation. Expressing this equality we have

$$p(v_2-v_1) = \int_{v_1}^{v_2} p\,dv.$$

Performing the integration this gives us

$$\frac{p(v_2-v_1)}{R\Theta} = \log\frac{v_2-a}{v_1-a} - \frac{27(a+\beta)}{8\Phi}\left(\frac{1}{v_1+\beta} - \frac{1}{v_2+\beta}\right) \quad . \quad . \quad (3)$$

For the sake of brevity let us write

$$\Pi = \frac{p}{R\Theta}, \quad \gamma = a+\beta, \quad W = v_2 - a, \quad w = v_1 - a;$$

with this notation the equations (1), (2), (3) become

$$\Pi=\frac{1}{w}-\frac{27\gamma}{8\Phi(w+\gamma)^2} \quad . \quad . \quad \text{(I)}.$$

$$\Pi=\frac{1}{W}-\frac{27\gamma}{8\Phi(W+\gamma)^2} \quad . \quad \text{(II)}.$$

$$\Pi(W-w)=\log\frac{W}{w}-\frac{27\gamma}{8\Phi}\left(\frac{1}{w+\gamma}-\frac{1}{W+\gamma}\right) \quad . \quad \text{(III)}.$$

These three equations furnish the solution of any problem concerning such a transformation.

If it is desired to determine Π, w, W as functions of Φ directly, we are led to a transcendental equation. It is consequently better to determine them all as well as Φ in terms of some other variable arbitrarily chosen. Thus for this purpose Planck used the transformation

$$W=r\cos^2\tfrac{1}{2}\phi, \quad w=r\sin^2\tfrac{1}{2}\phi\,;$$

but Clausius takes the new variable as

$$\lambda=\log\frac{W}{w},$$

which appears in equation (III). With this notation we obtain immediately from equations (I) and (II)

$$\frac{1}{w}-\frac{27\gamma}{8\Phi(w+\gamma)^2}=\frac{1}{W}-\frac{27\gamma}{8\Phi(W+\gamma)^2},$$

from which

$$\frac{27\gamma}{8\Phi}=\frac{(W+\gamma)^2(w+\gamma)^2}{Ww(W+w+2\gamma)}\,;$$

and substituting this in equation (I) we have

$$\Pi=\frac{1}{w}-\frac{(W+\gamma)^2}{Ww(W+w+2\gamma)}=\frac{1}{(W+w+2\gamma)}\left(1-\frac{\gamma^2}{Ww}\right).$$

Consequently equation (III) gives

$$\log\frac{W}{w}=\Pi(W-w)+\frac{27\gamma}{8\Phi}\left(\frac{1}{w+\gamma}-\frac{1}{W+\gamma}\right)=\frac{(W-w)(2Ww+W\gamma+w\gamma)}{Ww(W+w+2\gamma}.$$

But if

$$\lambda=\log\frac{W}{w}, \quad \text{we have} \quad W=we^{\lambda}.$$

Therefore

$$\lambda=(e^{\lambda}-1)\frac{2we^{\lambda}+\gamma(e^{\lambda}+1)}{e^{\lambda}[w(e^{\lambda}+1)+2\gamma]}.$$

Hence

$$w=\gamma\frac{1-2\lambda e^{-\lambda}-e^{-2\lambda}}{\lambda-2+(\lambda+2)e^{-\lambda}}$$

and

$$W=\gamma e^{\lambda}\frac{1-2\lambda e^{-\lambda}-e^{-2\lambda}}{\lambda-2+(\lambda+2)e^{-\lambda}}.$$

To calculate Π we substitute for w and W in the expression for it, and find

$$\Pi=\frac{e^{-\lambda}[(\lambda-2)+(\lambda+2)e^{-\lambda}][(1-e^{-\lambda})^2-\lambda^2e^{-\lambda}]}{\gamma(1-e^{-\lambda})(1-2\lambda e^{-\lambda}-e^{-2\lambda})^2}.$$

Finally we have

$$\Phi=\frac{27\gamma}{8}\,\frac{Ww(W+w+2\gamma)}{(W+\gamma)^2(w+\gamma)^2}=\frac{27}{8}\,\frac{[\lambda-2+(\lambda+2)e^{-\lambda}]\,[1-2\lambda e^{-\lambda}-e^{-2\lambda}]^2}{(1-e^{-\lambda})(\lambda-1+e^{-\lambda})^2(1-e^{-\lambda}-\lambda e^{-\lambda})^3}.$$

Each of these quantities may be expressed in a series of powers of λ. For

$$1-e^{-\lambda}=\lambda\left(1-\frac{\lambda}{\underline{|2}}+\frac{\lambda^2}{\underline{|3}}-\ .\ .\ .\right)$$

$$\lambda-1+e^{-\lambda}=\lambda^2\left(\frac{1}{\underline{|2}}-\frac{\lambda}{\underline{|3}}+\frac{\lambda^2}{\underline{|4}}-\ .\ .\ .\right)$$

$$1-e^{-\lambda}-\lambda e^{-\lambda}=\lambda^2\left(\frac{1}{\underline{|2}}-\frac{2\lambda}{\underline{|3}}+\frac{3\lambda^2}{\underline{|4}}-\ .\ .\ .\right)$$

$$\lambda-2+(\lambda+2)e^{-\lambda}=\lambda^3\left(\frac{1}{\underline{|3}}-\frac{2\lambda}{\underline{|4}}+\frac{3\lambda^2}{\underline{|5}}-\ .\ .\ .\right)$$

$$1-2\lambda e^{-\lambda}-e^{-2\lambda}=2\lambda^3\left(\frac{1}{\underline{|3}}-\frac{4\lambda}{\underline{|4}}+\frac{11\lambda^2}{\underline{|5}}-\frac{26\lambda^3}{\underline{|6}}+\ .\ .\ .\right)$$

$$(1-e^{-\lambda})^2-\lambda^2e^{-\lambda}=\lambda^4\left(\frac{1}{2\underline{|3}}-\frac{2\lambda}{\underline{|4}}+\frac{16\lambda^2}{3\underline{|5}}-\frac{12\lambda^3}{\underline{|6}}+\frac{99\lambda^4}{4\underline{|7}}\ .\ .\ .\right)$$

Hence

$$w=\gamma\left(2-\lambda+\frac{3\lambda^2}{2\,.\,5}-\frac{\lambda^3}{3\,.\,5}+\frac{17\lambda^4}{2^3\,.\,5^2\,.\,7}-\frac{\lambda^5}{3\,.\,5^2\,.\,7}+\ .\ .\ .\right)$$

$$W=\gamma\left(2+\lambda+\frac{3\lambda^2}{2\,.\,5}+\frac{\lambda^3}{3\,.\,5}+\frac{17\lambda^4}{2^3\,.\,5^2\,.\,7}+\frac{\lambda^5}{3\,.\,5^2\,.\,7}\ .\ .\ .\right)$$

Hence if we write

$$M=\gamma\left(2+\frac{3\lambda^2}{2\,.\,5}+\frac{17\lambda^4}{2^3.5^2\,.\,7}+\ .\ .\ .\right)$$

$$N=\gamma\left(1+\frac{\lambda^2}{3\,.\,5}+\frac{\lambda^4}{3\,.\,5^2\,.\,7}+\ .\ .\ .\right)$$

we have

$$w=M-N\lambda,$$
$$W=M+N\lambda.$$

From which we have

$$W+w=2M,$$
$$Ww=M^2-N^2\lambda^2.$$

Thence the sum and the product of W and w embrace only even powers of λ, and consequently Π and Φ only embrace even powers of λ. It follows, therefore, that in the neighbourhood of the critical temperature, when λ approaches zero, the quantities Π and Φ behave like the quantities W and w.

The foregoing equations determine w, W, Π, and Φ as functions of λ, and therefore in an indirect manner connect w, W, and Π with Φ. In researches the temperature Θ is ordinarily supposed to be given, and the pressure of the vapour and the specific volumes are required in terms of it. It is, therefore, desirable to express w, W, Π in terms of Φ. For this purpose Clausius writes

$$x=\sqrt{1-\Phi},$$

so that x vanishes, like λ, at the critical point, and the series for λ in terms of x becomes

$$\lambda=6x+3{\cdot}24x^3+2{\cdot}8801716x^5+2{\cdot}885628x^7+\ .\ .\ .$$

and by this means a table of values of λ was calculated for uniformly ascending values of Φ.

We have

$$\frac{dx}{d\Phi}=\frac{-1}{\sqrt{1-\Phi}}, \quad \frac{d(x^2)}{d\Phi}=-1.$$

The former is infinite at the critical point, while the latter remains finite, and a similar difference ought to exist between the derived functions of w, W, and Π. Hence at the critical point the specific volumes of the liquid and vapour experience changes which are infinitely great compared with the change of temperature, while the variation of the saturated vapour pressure bears a finite ratio to the change of temperature. This characteristic difference was also previously remarked by Van der Waals.

The form assumed by Clausius for the function Φ is

$$\frac{1}{\Phi}=\frac{a}{\Theta^n}-b,$$

and since $\Phi_c=1$, we have

$$a=\Theta_c{}^n(1+b),$$

so that the relation becomes

$$\frac{1}{\Phi}=(1+b)\left(\frac{\Theta_c}{\Theta}\right)^n-b.$$

In the case of carbonic acid $n=2$, and the equation reduces to the well-known form

$$p=\frac{R\Theta}{v-a}-\frac{C}{\Theta(v+\beta)^2}.$$

Clausius has compared this formula with the experiments of Regnault[1] on ether; from these he finds

$$a=2665, \quad b=0{\cdot}76786, \quad \text{and } n=1{\cdot}19233.$$

The table of vapour pressures calculated by means of the formula agrees very well with those obtained by experiment.

A comparison with Regnault's experiments on water gave

$$a=5210, \quad b=0{\cdot}85, \quad n=1{\cdot}24$$
$$\alpha=0{\cdot}00754, \quad \gamma=0{\cdot}001815.$$

The formula has been further compared by Professor G. F. FitzGerald[2] with the more recent experiments of Ramsay and Young on alcohol, and very fair agreement was found. Constant values of α and β did not, however, satisfy the observations accurately, for α varied from 1·087 at 0° C. to 0·184 at 240° C. Thus α diminished with rise of temperature, and it was also found to increase with increased pressure.

[1] *Relation des Expériences*, tom. ii. p. 393; and Sajotchewski (*Beiblatter*, vol. iii. p. 741, 1879).

[2] G. F. FitzGerald, *Proc. Roy. Soc.*, vol. xlii. p. 216, 1887.

Notwithstanding this, the formula of Clausius gives an exceedingly accurate general representation of the more important changes of state.[1]

224. The Critical Constants.—The critical constants, or the pressure, volume, and temperature at the critical point, may be easily obtained in terms of the constants which appear in the equation of Van der Waals. Writing this equation as a cubic in v, thus

$$pv^3-(bp+R\Theta)v^2+av-ab=0,$$

then at the critical point the three roots of this equation are equal. and hence the critical constants are determined by the equations

$$\begin{aligned} 3v_cp_c&=bp_c+R\Theta_c,\\ 3v_c^2p_c&=a,\\ v_c^3p_c&=ab. \end{aligned}$$

From the two last of these it follows at once, by division, that

$$v_c=3b$$

Hence

$$p_c=\frac{a}{27b^2},$$

and

$$\Theta_c=\frac{8a}{27Rb}.$$

In this manner Van der Waals, having determined the constants a and b from Regnault's experiments on the compressibility of carbonic acid, found for this substance $\theta_c=32°{\cdot}5$ C., the close agreement of which with the experimental result of Andrews is remarkable.

Taking one atmosphere as unit pressure, and the volume occupied by the gas at zero centigrade and one atmosphere pressure as unit volume, the values of the constants were

$$273R=1{\cdot}00646,\quad a=0{\cdot}00874,\quad b=0{\cdot}0023.$$

Treating the equation of Clausius (p. 421) in the same manner, we find the critical constants determined by the equations

$$3pv=p\alpha+R\Theta-2\beta p \qquad (1)$$
$$3pv^2\Theta=p\Theta\beta^2-2\beta\Theta(p\alpha+R\Theta)+c \qquad (2)$$
$$pv^3\Theta=c\alpha+\beta^2\Theta(p\alpha+R\Theta) \qquad (3)$$

---

[1] M. Sarrau (*Comptes Rendus*, tom. ci. p. 941, 1885) employs the exponential form $\Phi=ke^{\Theta}$ in the formula of Clausius, and M. Battelli used the equation in the more general form

$$p=\frac{R\Theta}{v-\alpha}-\frac{a\Theta^{-m}-b\Theta^{-n}}{(v+\beta)^2}.$$

Substituting in the second the value of $p\alpha + R\Theta$ found from the first, viz. $p(3v + 2\beta)$, we obtain

$$3p\Theta(v+\beta)^2 = c \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

and making the same substitution in (3) we obtain

$$c\alpha = p\Theta(v^3 - 3v\beta^2 - 2\beta^3) = p\Theta(v-2\beta)(v+\beta)^2 \qquad . \quad . \quad . \qquad (5)$$

Now equation (4) may be written in the form

$$3p = \frac{c}{\Theta(v+\beta)^2} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Hence at once by the original equation we have

$$4p = \frac{R\Theta}{v-\alpha} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

Now (4) and (5) give at once

$$v_c = 3\alpha + 2\beta,$$

and hence by multiplication of (6) and (7) we find

$$p_c = \sqrt{\frac{cR}{216(\alpha+\beta)^3}}.$$

Hence

$$\Theta_c = \sqrt{\frac{8c}{27R(\alpha+\beta)}}.$$

These results may also be easily obtained by expressing that at the critical point

$$\frac{dp}{dv} = 0,$$

and also

$$\frac{d^2p}{dv^2} = 0.$$

Applying this method to the equation

$$\frac{p}{R\Theta} = \frac{1}{v-\alpha} - \frac{1}{\Psi(v+\beta)^2},$$

where Ψ is a function of Θ, we have from

$$\frac{dp}{dv} = 0$$

the equation

$$\frac{1}{(v-\alpha)^2} = \frac{2}{\Psi(v+\beta)^3} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

while

$$\frac{d^2p}{dv^2} = 0$$

gives

$$\frac{2}{(v-\alpha)^3} = \frac{6}{\Psi(v+\beta)^4} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Dividing (1) by (2) we obtain at once the critical volume

$$v_c = 3\alpha + 2\beta,$$

and substituting this value of v in (1) or (2) we find

$$\Psi_c = \frac{8}{27(\alpha+\beta)},$$

which, substituted in the original equation with v_c, yields

$$\frac{p_c}{R\Theta_c}=\frac{1}{8\gamma}.$$

The above value of Ψ_c shows why it is necessary to write the equation in the form

$$\frac{p}{R\Theta}=\frac{1}{v-\alpha}-\frac{27(\alpha+\beta)}{8\Phi(v+\beta)^2}$$

if it be desired to have Φ a function of Θ, which equals unity at the critical temperature.

225. Corresponding States.—A deduction of Van der Waals's from his equation concerns what may be termed corresponding states of matter. If the pressure, volume, and temperature of a substance be expressed as multiples of their critical values—that is, if we write

$$p=\lambda p_c, \quad v=\mu v_c, \quad \Theta=\nu\Theta_c,$$

then any other substance will be in a corresponding state when its pressure, volume, and temperature are the same multiples λ, μ, ν of their critical values. Substituting in the equation

$$\left(p+\frac{a}{v^2}\right)(v-b)=R\Theta,$$

and replacing p_c, v_c, Θ_c by their values in terms of a, b, R, we have

$$\left(\lambda+\frac{3}{\mu^2}\right)(3\mu-1)=8\nu,$$

an equation in which everything depending on the nature of the substance has disappeared, and which should apply to all substances, just as $pv=R\Theta$ applies to all perfect gases. Hence if pressures, volumes, and temperatures be expressed in terms of their critical values, the isothermals become the same for all substances.

At the time when Van der Waals published his work sufficient experimental data were not available to test the accuracy of these deductions, and since that time they have been subject to much criticism, both favourable and adverse.[1] From the recent experiments of Dr. S. Young,[2] it appears that the conclusions of Van der Waals are very approximately true for the halogen derivatives of benzine, or at least that these substances show very much smaller deviations than the others examined. The law, therefore, seems to be not quite, but very nearly, true for these substances; but in the case of the other sub-

[1] A discussion of this equation, in which Lord Rayleigh, Professor P. G. Tait, and Professor Kortweg took part, appeared recently in *Nature*, vols. xliv. and xlv., 1891-92.

[2] S. Young, *Phil. Mag.*, vol. xxxiii. p. 153, 1892.

stances examined the majority of the generalisations were either only roughly true or else altogether disobeyed.

Examples

1. Employing Leray's equation (p. 74), deduce the equations of Van der Waals and Clausius.

[If in the equation

$$pv=\frac{2}{3}na\Theta\left(1+\frac{c}{v}\right)$$

we replace n by $n_0(1-ep)$, which expresses that n decreases as the pressure increases, and if we suppose c and e so small that their squares may be neglected, we have

$$p/(1-ep)=p+ep^2, \quad \text{and } v/\left(1+\frac{c}{v}\right)=v-c;$$

and hence

$$(p+ep^2)(v-c)=\frac{2}{3}an_0\Theta.$$

Replacing p^2 by the approximate value k/v^2, and writing $R=\frac{2}{3}an_0$, we have

$$\left(p+\frac{k}{v^2}\right)(v-c)=R\Theta,$$

which is Van der Waals's equation.

If, however, we also take account of the variations of temperature and write

$$n=n_0\left(1-\frac{ep}{\Theta}\right),$$

the formula becomes

$$\left(p+\frac{ep^2}{\Theta}\right)(v-c)=R\Theta,$$

and as p does not vary exactly as the inverse of v, it may be taken more approximately as the inverse of $(v+\beta)$, and we obtain

$$\left[p+\frac{k}{\Theta(v+\beta)^2}\right](v-c)=R\Theta,$$

which is the equation of Clausius.

Finally, if we write $n=n_0\left(1-epe^{-\Theta}\right)$, we obtain the formula of M. Sarrau—

$$p=\frac{R\Theta}{v-c}-\frac{ke^{-\Theta}}{(v+\beta)^2}.\Big]$$

2. Using the notation of Art. 57, show that the ratio of the specific heats of a gas may be expressed in the form

$$\gamma=1+\frac{2a}{3(1+a+b)}.$$

[Assuming the equation $pv=\frac{1}{3}\bar{u}^2$, we have

$$pdv+vdp=\frac{2}{3}\bar{u}d\bar{u}.$$

But if the transformation is adiabatic, the external work done is equal to the whole change of energy of the gas, and therefore (Art. 57)

$$-pdv = \overline{u}d\overline{u} + \overline{v}d\overline{v} + \overline{\omega}d\overline{\omega}$$

$$= \left(1 + \frac{1}{a} + \frac{b}{a}\right)\overline{u}d\overline{u}.$$

Hence

$$vdp + \left\{1 + \frac{2a}{3(1+a+b)}\right\} pdv = 0,$$

or

$$pv^{1+\frac{2a}{3(1+a+b)}} = \text{constant.}]$$

CHAPTER VI

RADIATION AND ABSORPTION

SECTION I

GENERAL THEORETICAL CONSIDERATIONS

226. Propagation of Heat.—There are three methods commonly recognised by which heat may be propagated or conveyed from one place to another. The first of these is that which we are about to consider at present, and is termed *radiation*. It is by this method that heat and light reach us from the sun, or from a lamp or fire, and during the period of transit the heat is spoken of as radiant heat, or simply as radiation, this term embracing light as well as heat. This method of propagation is distinguished from the other two, known as convection and conduction, in which the transfer of heat is effected wholly or largely by the agency of matter. In the former the heat is carried from place to place by the matter with which it is associated, so that the flow of heat depends altogether on the motion of matter. It is by this method that heat is conveyed through buildings heated by hot water pipes, and it is chiefly in this way that uniformity of temperature is established in unequally heated fluids.

The process of conduction, on the other hand, does not depend on any visible motion of matter. It is by this method that temperature equilibrium is established in solids, and that heat passes from the warmer to the colder parts of the same solid. Thus if one end of an iron bar be placed in a furnace, and the other in a vessel of ice, a flow of heat will take place along the bar from the furnace to the ice; and if radiation from the sides of the bar be prevented as far as possible, the rate at which the ice melts will afford a rough measure of the flow of heat along the bar. This method of conveying heat from one place to another is usually attributed to molecular action or propagation by contact, the warmer molecules heating the colder by contact or otherwise. This process, however, will be considered in fuller detail in the next chapter; at present we shall confine our attention to the process of radiation which does not appear to depend in any way on the presence of matter, but which takes place through the best

vacua, and through interstellar spaces, and is further distinguished from the comparatively slow processes of convection and conduction by advancing with the enormous velocity of 300,000,000 metres per second.

In approaching the study of such a subject as the nature of radiant heat, and the process by which it is emitted and propagated through space, the most philosophic method of procedure is to determine as far as possible the laws which govern its propagation through different media, as well as its passage from one medium to another, before any hypothesis is framed as to the nature of the emission or the mechanism by which it is propagated. Thus, without any hypothesis, the laws of its reflection and refraction, and the manner in which its intensity varies with the distance from the source, may be examined and determined. Whatever the mechanism may be by which radiant heat is emitted and propagated, we have the most complete experimental evidence that the process is precisely the same as that employed in the propagation of light, and any evidence which can be adduced in favour of the supposition that light is a wave motion propagated through a medium can also be stated with regard to heat. Radiation in this sense consists essentially in the propagation of a wave motion through the ether. What is propagated and radiated in all cases is energy, and all phenomena connected with it are to be explained as the consequences of the interchange of energy between the ether and matter, and it is purely as the recipients or donors of such that we ourselves become sensible of heat and cold.

227. On the Formation of a Theory.—The phenomena of radiant heat and light having been proved to be subject to the same laws of reflection, refraction, polarisation, and interference—in fact, the two being reducible to, and merely different effects of, the same physical agency—a definite hypothesis is framed, and the investigation proceeds from the direct study of the phenomena to the elaboration of a connected theory which accounts for the facts, and exhibits their sequence and relations. The existence of atoms and molecules of matter is first admitted, and a medium is then assumed in which they vibrate and generate waves, or a periodic disturbance of some sort, travelling with the enormous velocity of 300,000,000 metres per second. In this manner a mental picture is formed of the unknown process by which energy is emitted by a body and propagated through the space around it—a picture which has proved of enormous advantage in grappling with the investigation of the phenomena, but which may, or may not, have a similitude to the processes actually in action.

In forming such a picture, or in framing any hypothesis as to the

mode of propagation of radiant heat and light, we fall back upon analogous phenomena which we can thoroughly examine, and with the ideas formed in the study of the latter, we approach the investigation of the former. We thus proceed to the interpretation of the unknown processes in terms of well-conceived analogies derived from the known. The ideas by which we picture and conceive of the propagation of heat and light are derived from the study of the phenomena of sound. A sounding body is the source of an influence which is radiated from it in all directions through the surrounding medium with a definite velocity. When this phenomenon is examined, it is found that the sounding body is in rapid vibration, and that these vibrations are communicated to the air, that sound waves are thus generated in the air which spread out from the vibrating body and break upon the ear, causing the impression which we call sound. Here the vibrating body is recognised as the source of an influence which is radiated from it in all directions with a definite velocity, and which causes a certain impression on one of our organs of sense. With the knowledge thus gained, we proceed to the explanation of the phenomena of heat and light, and make the very promising and attractive assumption that they too are due to wave motion propagated through a hypothetical medium named the ether.

In this case, however, as the nature of the medium is entirely unknown, as well as the exact character of the waves, we consider it prudent in the present state of knowledge to stop at this stage of the hypothesis, and we hesitate to ascribe any particular type or character to the vibrations and wave motion. In one respect, however, the study of light seems to restrict the character of these waves. It appears from the consideration of certain phenomena that they cannot be propagated by longitudinal vibrations, as in the case of sound, or at least that such vibrations do not play an essential part in the production of light or vision. With this one restriction, we make no further hypothesis, except for particular purposes of explanation and illustration. We have distinct evidence that the propagation is that of a periodic disturbance or a periodic change of some property of a medium; but beyond this no other assumption is warranted by the facts, except for the purposes of working out some particular theory, and the extra assumptions thus introduced should be clearly laid down as the hypotheses on which the theory is built, and these are justified only in so far as all the deductions following from the theory are substantiated by direct appeal to experiment.

228. Dynamical Analogy.—Let us now consider the radiation and absorption of sound, in order that we may approach the analogous

phenomena of light and heat with a distinct mental picture which will be exceedingly convenient and fruitful, but which at any stage may be modified or entirely discarded when it is found to be misleading or inconsistent with the new facts. Let us suppose that we have two mounted tuning-forks of the same pitch placed in air and at a distance from each other. If one of the forks is set in vibration, the waves which it radiates through the air fall upon the other, and set it also in vibration, because they are of the same period as those waves which it would itself emit when sounding. Thus, while one is losing energy the other is gaining it, or as we might put it with reference to the other radiation, while one is growing colder the other is growing warmer. That the second fork absorbs the radiation emitted by the first may be distinctly placed in evidence by stopping the vibration of the first, in which case the sound emitted by the second can be distinctly heard, although at the beginning of the experiment it was silent. It has consequently been set in vibration by the waves emitted by the other fork. Here, then, we have a distinct case of radiation and absorption of sound, the essential condition for absorption being that the pitch of the absorbing fork should be the same as that of the emitting. This single principle permeates the whole science of radiation and absorption, and is embraced in the general statement that a body absorbs waves which are of the same period as those which it emits when it is itself in vibration.

In order to apply this idea more comprehensively to the case of radiant heat and light, it is necessary to take into account the supposed molecular structure of matter. We must, from this point of view, not merely regard a radiating body as analogous to a single tuning-fork, but rather as a swarm of tuning-forks, each molecule corresponding to a fork in vibration, and emitting waves peculiar to itself. If the forks of such a swarm be relatively fixed and not entangled, the waves radiated from the system will depend only on the periods of free vibration of the forks; but if the forks be not relatively fixed, but have motions of translation amongst each other, such as has been ascribed to the molecules of a fluid, the waves radiated will be influenced both by the motion of the forks and by their mutual collisions, the pitch of those forks which are moving at any instant towards the observer will be somewhat raised, while that of those which are moving away from the observer will be lowered. For this reason, if the forks are all identical and possess the same free period, the sound emitted by the moving system will not be a pure tone, of a single wave-length, but will consist rather of a group of waves lying within certain limits determined by the velocity of motion of the forks, some of the waves

being longer and some shorter than that emitted by a single fork at rest. It is in this manner that the finite width of the spectral lines of an incandescent gas has been explained.[1] Instead of having a line representing a single wave-length of light, we are presented with well-defined narrow bands arising from the broadening of the lines already referred to by the motions of translation of the molecules of the radiating substance. The same motion promotes the absorption of groups of waves rather than of waves of a single period, so that the absorption bands are also of finite width.

If now the radiation from such a system of vibrating forks falls upon another system in silence, any waves which are of the same period as those peculiar to the second system will be absorbed by it, and the forks of this system will be set in vibration. This absorption will continue till an equilibrium is established between the rate at which the energy is absorbed and emitted by the second system. This corresponds exactly to the method by which a cold body is supposed to become warmed in the presence of a hot one. The temperature of one falls by radiation, while that of the other rises by absorption until an equilibrium is established between the radiation and absorption of each. From this point of view every body at a stationary temperature must be regarded as radiating energy at a constant rate; but since the temperature remains stationary, it must be regarded as also absorbing energy at the same rate, so that, on the whole, the loss by radiation is exactly compensated by absorption from other sources. The equilibrium here attained is not one of rest but rather one of activity, such as exists between a liquid and its saturated vapour in a closed space when the stage is reached at which as many molecules return to the liquid per second as are projected from its surface. In this case too there is an equilibrium; but there is also constant evaporation balanced by an equal condensation, and matters remain as if the equilibrium were one of death rather than one of active life.

It may be remarked here that a large swarm of similar tuning-forks, such as we have just considered, would be highly opaque to a note or sound wave of the same period as themselves, for they rapidly absorb such a wave, and it would be almost completely used up before it had penetrated far into the system. In analogy to this it was discovered by De la Roche, and abundantly confirmed by Melloni and others, that when radiant heat is passed through one screen the transmitted beam is almost completely transmitted by another screen of the same material, and it has also been established that all substances are highly opaque to their own radiation.

[1] See the author's *Theory of Light*.

229. The Theory of Exchanges.—The foregoing considerations prepare us to grant that each body whose molecules are in vibration is a source of radiation in the ether, and that the amount of radiation thrown off in this manner by any body depends only on the nature and temperature of the body itself. Returning again to the system of vibrating tuning-forks, we may admit that the sound-radiation from each fork takes place independently of all the others. Each fork is in vibration, and must be regarded as the centre of a system of waves as if all the others were at rest. The rate at which any fork parts with its energy may be, however, considerably modified. Thus if two or more of the forks happen to be of the same pitch, each will absorb part of the energy emitted by the other and will thus recruit its stock, so that the energy lost per second by any fork will now be only the difference between that radiated through its own vibration and that absorbed from the others. When these two parts are equal the energy of the fork remains constant; but still we regard it as radiating at a constant rate, while it absorbs at the same rate, and it is in this sense that the radiation of any body at any temperature is said to be equal to its absorption at the same temperature.

In this manner we are led to believe that the equilibrium of temperature which ultimately becomes established among a system of bodies contained in an enclosure impervious to heat, and which contains no source of heat, is attained not merely by the warmer bodies radiating to the colder, but by a mutual process of radiation and absorption, all the bodies being supposed to radiate simultaneously each to an amount depending on its constitution, surface-condition, and temperature. Further, when the equilibrium of temperature is once attained, the process of radiation is not supposed to cease, but to continue as actively as before, equilibrium being maintained by simultaneous radiation and absorption.

From this point of view there is a continual interchange of energy between the bodies within the enclosure, while at the same time the energy of each remains constant. Before equilibrium is reached the hotter bodies radiate more than they absorb, while the colder absorb more than they radiate; the quantity which each radiates per second at any stage is, however, independent of whether its temperature happens to be rising or falling, and is supposed to be determined by the nature and temperature[1] of the body.

This view was introduced by Prévost[2] of Geneva in 1792, when

[1] On this point see *Phil. Mag.*, October 1881, p. 261, Arthur Schuster.

[2] Prévost, *Sur l'Equilibre du Feu*, Genève, 1792; *Du Calorique Rayonnant*, Gen., 1809.

endeavouring to explain the supposed radiation of cold.[1] According to Prévost's line of thought any body is not merely regarded as radiating heat when its temperature is falling, or absorbing heat when its temperature is rising. What it is wished to express is that both processes are continually and simultaneously going on, the radiation depending only on the body itself, while the absorption depends on the nature of the body itself as well as on the condition of neighbouring bodies.

In order to illustrate this point let us consider the case of a thermometer suspended in a warm room at a steady temperature. In this case all the bodies in the room are radiating heat, part of which is absorbed by the thermometer, and if the temperature of the thermometer is stationary, the quantity of heat absorbed by it is balanced by an equal radiation. If now a cold body be brought into the room and placed in the vicinity of the thermometer, this body will screen the thermometer from some of the radiation which previously fell upon it, and will not itself radiate an equal supply. The total radiation received by the thermometer will consequently be diminished. The equilibrium which previously existed will thus be broken, and the temperature of the thermometer will fall to that point at which its emission is precisely equal to its absorption under the new circumstances. This is a case of what was designated as the radiation of cold. It illustrates how equilibrium is reached and maintained, not merely by the warmer bodies radiating and the colder absorbing, but rather by the mutual process of simultaneous emission and absorption.

It also illustrates how largely the indications of a thermometer depend on the nature of the radiation of the bodies around it as well as on the temperature of the medium in which it is immersed. The indication of a thermometer may differ very much from the temperature of the air at the point where it is suspended. If the waves emitted by any neighbouring body are such as the thermometer can absorb, it will be influenced by them in a corresponding degree; but if they are such as it does not absorb—that is, if they are dissimilar to those which it emits, then they will be without influence on the indications of the instrument. Whether a thermometer detects a certain class of waves or not depends on the nature of the material, thus if the thermometric substance absorbs only waves of a certain length, then it will respond only to these waves, and although it may be traversed by

[1] The experiment illustrating the reflection of cold was revived by Pictet, but was originally made some centuries before by Plempius, and the Academicians del Cimento.—Young's *Lectures*, p. 489.

Thermometers special indicators.

copious radiation of other wave-lengths, its indication might still be the absolute zero of temperature. The indication of a thermometer is thus determined by the resultant effect of all the various waves which influence it.

The indication of a thermometer is found to be ultimately the same in all parts of an enclosure impervious to heat, and which contains no source of heat; and it is in this statistical sense that we assert that all parts of, and all objects in, such an enclosure ultimately come to the same temperature. The indication of the thermometer is independent of the shape or material of the walls of the enclosure, and if the bulb be coated with lamp-black, or silver-foil, or any other substance, the temperature recorded will remain the same. Now, of the whole radiation falling upon the thermometer in such a case, part is absorbed and part is reflected either regularly or irregularly. The reflected part when the bulb is silvered is enormously greater than when it is coated with lamp-black, and consequently the absorbed portion must be so much less in the former case than in the latter. But since the temperature of the thermometer is the same whatever it be coated with, it follows that the heat absorbed by it when coated with any substance must be exactly the same as that emitted, and hence the emission of any substance at any temperature must be exactly equal to its absorption at the same temperature. If we confine our attention to a body A, then when the flow of heat takes place from the surrounding space B into A, we say that A is absorbing heat from B; but if the flow takes place from A to B, we say that A is radiating, or, if we like, that B is absorbing heat from A. The direction of the flow, then, determines whether we say that a body is emitting or absorbing heat, and the assertion of the equality of the emitting and absorbing powers assumes that for the same infinitesimal difference of temperature the flow will be the same whether it takes place from A to B or from B to A, across the surface of separation.

230. Emissivity or Surface Conductivity.—It was established by Sir John Leslie, by his researches in radiant heat, that some substances emit heat under the same conditions much more copiously than others. For this reason it is customary to speak of the emissivity or emissive power of a substance or of the surface of a body. The radiating body employed by Leslie was a cubical vessel of block-tin, filled with hot water, the sides of which could be coated with any substance whose emissivity it was desired to study. This vessel is known as Leslie's cube. It is constructed so that it may be rotated round a vertical axis, and any face can be brought into action when desired. If the cube be filled with hot water, and if one side be coated with a thin

sheet of gold, another with polished silver, a third with copper, and the fourth with varnish, it is found, when these faces are allowed to radiate in succession against the face of a thermopile or other delicate radiometer, that the faces coated with the metals radiate only very feebly; but when the varnished face is turned towards the pile, the indication of the instrument shows that the radiation from this face is very copious. The polished metals are consequently much less efficient as radiators than the varnish. It is for this reason that hot liquids contained in polished metal vessels retain their heat much longer than when the surface is unpolished. The reflection at the surface increases with the polish, and this whether the radiation is passing from the inside outwards or from the outside inwards. The polished surface is a good reflector, and therefore a poor radiator.

Without adopting any hypothesis as to the process by which radiation occurs, or as to the nature of heat or the structure of matter, the *surface emissivity* of body may be defined as measured by the quantity of heat which a body loses per unit surface per unit time under given conditions—such, for example, as when its temperature is 1° C. higher than that of the enclosure in which it is situated, and when the air in this enclosure is at a definite pressure or entirely removed. This definition does not involve reference to the radiation of any other body, nor does it involve any hypothesis as to the law of variation of emissivity with temperature, but leaves its dependence on temperature and other circumstances to be determined by direct experiment.

This quantity is also termed the *surface conductivity*, and sometimes the *external conductivity*, as distinguished from the internal conductivity or property by which heat is conveyed through solids from places of higher to places of lower temperature. In practice all we can determine is the rate at which a body loses heat when cooling under given conditions, so that the so-called coefficients of emission which have been as yet determined, are only rough measurements involving what might be termed the emissivity proper of the substance as well as the internal conductivity of the material and other quantities depending on the nature of the enclosure.

SECTION II

COOLING

231. Empirical Laws of Cooling.—When a hot body is suspended in the air it is easily determined that the cooling proceeds by two very distinct processes which act simultaneously. One of these is the radiation already considered, which takes place equally in all directions, and the other arises in the convection and conduction of the air surrounding the body. The air in immediate contact with the body becomes heated and rises through the colder and denser air above. In this manner an ascending current of air is established around the body, and fresh supplies are continually brought into contact with it beneath, which become heated in turn, and rising carry off part of its heat. This is the process termed convection, and the amount of heat carried off in this manner will depend on the pressure and nature of the air or gas in which the body may be immersed. The rate of cooling will consequently be determined by the sum of two functions, one of which represents the loss of heat by radiation, and the other that lost by the convection and conduction of the surrounding medium.

For the sake of simplicity we shall first consider the case of a body suspended in an enclosure which is free from air or other gas, so that the cooling takes place by radiation to the walls of the enclosure alone. If the temperature of the body be θ, the heat lost per second by radiation will be some function of the temperature θ; and if the walls of the enclosure be maintained at some temperature θ_0, then by the considerations reviewed in the last section a mutual process of radiation and absorption takes place between the body and the walls of the enclosure. The heat absorbed per second by the body will be a function of the temperature θ_0 of the walls of the enclosure, and this quantity will be the same as that which would be radiated by the body at θ_0, for at this temperature there would be equilibrium of temperature between the body and the enclosure.

Hence, if $f(\theta)$ denotes the heat lost per second by radiation when the body is at the temperature θ, the same function will represent the heat gained by absorption when in an enclosure at the same temperature, since by the theory of exchanges the radiation at any temperature is equal to the absorption at the same temperature. Hence, if $f(\theta)$ represents the rate of loss by radiation, $f(\theta_0)$ will represent the rate of gain by absorption,[1] and their difference

$$f(\theta)-f(\theta_0)$$

will determine the rate of cooling of the body.

Newton seems to have been the first to consider the law of cooling of a body subject to any constant cooling action—such, for example, as the influence of a uniform current of air. In such cases he supposed that the rate of cooling was proportional to the excess of the temperature of the body above that of the medium in which it was immersed. This admission amounts to assuming $f(\theta) = \mathrm{A}\theta + \mathrm{B}$ in the foregoing expression, or if the temperature be measured from the absolute zero, then $\mathrm{B} = 0$, and the assumption is that the total radiation of a body is proportional to its absolute temperature. In this case we have for the rate of cooling—

$$f(\theta)-f(\theta_0)=\mathrm{A}(\theta-\theta_0),$$

or since the rate of cooling is $-\dfrac{d\theta}{dt}$,

we may write

$$\frac{d\theta}{dt}=-\mathrm{E}(\theta-\theta_0),$$

where E is a coefficient depending on the nature of the body and its surface condition. This formula has been found to represent the facts fairly well for small differences of temperature, and may be used to determine the radiation correction in such experiments as ordinarily occur in calorimetry, where the excess of θ over θ_0 never exceeds a few degrees centigrade. For differences exceeding 40° or 50° C., this law was found even by such early experimenters as Martine,[2] Kraft, Richmann, Leslie, and Dalton to deviate seriously from the truth when temperature is measured in the ordinary way by a mercurial thermometer, and Dalton for this reason proposed a new scale of temperature, according to which the law of Newton would be exact.

In consequence of these discrepancies Dulong and Petit undertook an elaborate series of experiments on the cooling of thermometers in an enclosure maintained at a constant temperature, and which

[1] This is the assumption.

[2] *Dissertations sur la Chaleur*, 1740.

could be either exhausted or filled with a gas at any pressure desired. From the results of these experiments they were led to propose the formula $Aa^{\theta}+B$ for $f(\theta)$, the rate of radiation of a surface at temperture θ. In this formula θ may be taken as the absolute temperature if desired, as the effect is only to alter the value of the coefficient A. If the absolute temperature be chosen, then the radiation will be zero when $\theta=0$ and we will have $B=-A$. By the same reasoning as before it will follow that the absorption from the walls of the enclosure at θ_0 will be $Aa\theta_0+B$, so that the rate of cooling will be

$$f(\theta)-f(\theta_0)=A(a^{\theta}-a^{\theta_0}),$$

or

$$\frac{d\theta}{dt}=-E(a^{\theta}-a^{\theta_0}).$$

In the same memoir[1] Dulong and Petit have investigated the rate of cooling under the simultaneous action of radiation and convection, and have represented it by an empirical formula of a highly artificial character. The term representing the loss by radiation being the same as that given above, while that which represents the loss by convection and conduction depends on the pressure of the gas, being jointly proportional to a power of the pressure varying with the nature of the gas and a power of the temperature excess which is the same for all gases. The formula of Dulong and Petit seems to apply with considerable accuracy through a much wider range of temperature difference than that of Newton. We shall consequently review the experiments by which they were led to the law which bears their name. It may, however, be remarked here that our knowledge of the loss of heat by radiation is very scanty, and with regard to convection we are in almost complete ignorance except in some of its special applications, for here we are presented with difficulties of a more imposing order than those which are encountered in many hydrokinetic problems, of which we have as yet obtained only approximate solutions.

Dulong and Petit's Experiments

232. Principles of the Research.—In their classical investigations of the laws of cooling, MM. Dulong and Petit operated entirely by observing the rate of cooling of large liquid-in-glass thermometers under various conditions. In studying the influence of the nature of the surface on the rate of cooling the advantage of using a liquid which

[1] Dulong and Petit, *Ann. de Chimie et de Physique*, 2e, tom. vii. pp. 225 and 337, 1817.

is a good conductor is twofold. In the first place, when the temperature of the outside layer falls, convection currents are set up which equalise the temperature of the mass, and the greater the conductivity of the liquid the more rapidly will this equality be attained. For this reason the temperature of a good conducting liquid like mercury will be approximately the same throughout, and the rate of cooling will depend chiefly on the nature of the surface of the bulb, and this can be varied at pleasure.

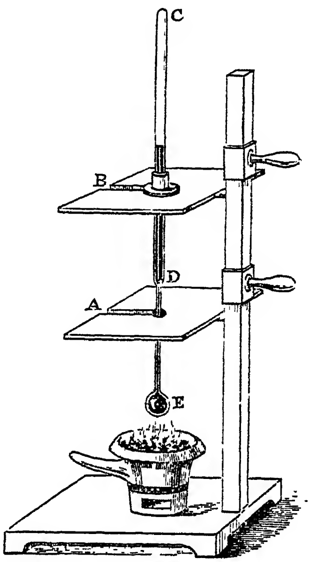


Fig. 123.

The thermometers employed by Dulong and Petit in this research were constructed after the fashion represented in Fig. 123. Each was provided with a large bulb E and a wide stem CD joined together by a tube DE of capillary bore, which prevented convection currents passing between the liquid in the bulb and that in the stem. In making an experiment the bulb alone was heated, while the stem was screened, so as to be always as nearly as possible at the temperature of the air, and on account of the width of the upper portion of the stem, the bulb, even though large, could be heated if necessary almost to the boiling point of mercury. During the process of cooling, the cold mercury from the stem enters the bulb and lowers the temperature of the mass within the bulb, so that the apparent velocity of cooling is rendered too high. Hence all observations had to be corrected for this inequality of temperature.

The main object of the inquiry was to determine the velocity of cooling of any body under given conditions as a function of the temperature. Thus, if the rate of cooling be expressed by the equation

$$-\frac{d\theta}{dt}=f(\theta) \qquad (1)$$

the object is to determine the form of the function f, the temperature of the enclosure being given. From an experimental point of view, ever, it is easier to express the temperature of the body at any as a function of the time. Thus, if we have

$$\theta=\phi(t) \qquad (2)$$

then by differentiating (2) and comparing with (1), we see that

$$f(\theta) = -\phi'(t),$$

or the velocity of cooling is the first derived of the function ϕ.

In order to determine this function Dulong and Petit, having heated the thermometer, placed it under the conditions in which its cooling was to be studied, and they observed its temperatures

$$\theta_0, \theta_1, \theta_2, \theta_3, \quad \ldots \quad \theta_n,$$

at the times

$$0, t_1, t_2, t_3, \quad \ldots \quad t_n.$$

From these observations they concluded that the temperature at any time could not be found by the simple formula of Newton, but by the more general expression

$$\theta = \theta_0 a^{\alpha t + \beta t^2} \qquad (3)$$

where θ is the excess of the temperature of the thermometer over that of the enclosure at the time t, θ_0 the excess at the beginning of the experiment, $t=0$, and a, α, β are constants which can be determined by a knowledge of any three values of θ at the corresponding times.

Differentiating (3) we have

$$\frac{d\theta}{dt} = \theta(\alpha + 2\beta t) \log a \qquad (4)$$

and by eliminating t between (3) and (4) the velocity of cooling is determined as a function of the temperature excess θ.

In order to diminish the time of observation in this investigation two thermometers were used. The larger, having a bulb of 6 cm. diameter, was used at high temperatures, and the smaller, with a bulb of 2 cm. diameter, was employed for the lower temperatures, the observations with the smaller being commenced at a temperature somewhat above that at which those with the larger were stopped.

233. Preliminary Experiments.—The various circumstances which may influence the rate of cooling of a thermometer placed in a vacuum are, the form and extent of the surface of the bulb as well as its nature or coefficient of emission, the total mass and nature of the liquid enclosed in the bulb, and finally the temperature θ_0 of the enclosure, as well as the excess of $\theta - \theta_0$ of the thermometer. If, however, the thermometer be suspended in a gas, the rate of cool[illegible] will be influenced by the conduction and convection of the gas. this case, then, the whole velocity of cooling will be the sum o functions, one of which determines the cooling by radiation

walls of the enclosure, and the other the cooling action of the gas. The latter will be influenced by all the circumstances mentioned above, and in addition by the nature and pressure of the gas. Besides this, the rate of cooling will depend on the magnitude and shape of the enclosure, as well as upon the nature of its walls, and the rate of cooling for one species of radiation may, in a given enclosure, be very different from that for another. These considerations have not, however, been investigated by Dulong and Petit.

Writing the total velocity of cooling in the form

$$V=f(M, N, S, E, \theta_0, \theta-\theta_0)+\phi(M, N, S, E, \theta_0, \theta-\theta_0, p, G),$$

where M and N refer to the mass and nature of the liquid respectively, S the area of the surface of the bulb, and E its coefficient of emission, θ_0 the temperature of the enclosure, and θ that of the thermometer, p the pressure, and G the nature of the gas, Dulong and Petit proceeded by some preliminary experiments in air to test how far the rate of cooling was influenced by the mass M and nature N of the liquid, and by the surface S of the bulb. Taking three thermometers with bulbs 2, 4, 7 cm. respectively in diameter, and consequently differing in mass M and surface area S, their cooling in air at θ_0 was noted, and their velocities of cooling, V_1, V_2, V_3, were calculated by the formula of the preceding article.

It will be seen from the following table that these velocities diminish as the mass increases, but that their ratios remain the same whatever be the excess of temperature. This proves that the velocities of cooling of the different thermometers may all be expressed by some function of M and S, multiplied by a function of the other variables, which is the same for all the thermometers.

INFLUENCE OF M AND S

$\theta-\theta_0$.	V_1.	V_2.	V_3.	V_1/V_2.	V_1/V_3.
100	18·92	8·97	5·00	2·11	3·78
80	14·00	6·60	3·67	2·12	3·81
60	9·58	4·56	2·52	2·10	3·80
40	5·93	2·80	1·56	2·12	3·80
20	2·75	1·30	0·73	2·11	3·77

I. exactly the same manner Dulong and Petit studied the influence nature of the liquid and of the form of the containing vessel,

To find the effect of the form of the vessel it was necessary to employ bulbs of different shapes—one spherical and the other cylindrical, made of the same material, and filled with the same liquid, were used. To determine the effect of the nature of the liquid it was necessary to observe the cooling of the same bulb filled with different liquids (mercury, alcohol, and water were used). Dulong and Petit then calculated the rates of cooling for equal excesses of temperature, and found that these bear constant ratios to each other, as indicated in the following table :—

INFLUENCE OF THE NATURE OF THE LIQUID

Excess, $\theta - \theta_0$.	Mercury, V_1.	Water, V_2.	V_2/V_1.
60	3·03	1·39	0·458
50	2·47	1·13	0·452
40	1·89	0·85	0·450
30	1·36	0·62	0·456

Similar tables are given in which mercury is compared with alcohol and with sulphuric acid, and these lead to the same conclusion. These experiments show that the total rate of cooling may be expressed as the sum of two functions, one a function of E, θ, $\theta - \theta_0$, and the other a function of these quantities, as well as of p and G, both of these functions being also multiplied by the same quantity A, which is itself a function of the mass and nature of the liquid, and of the surface S of the bulb. The expression for the rate of cooling thus becomes simplified into the following form :—

$$V = Af(E, \theta, \theta - \theta_0) + A\phi(E, \theta, \theta - \theta_0, p, G).$$

The remaining variables do not submit to the same simplification. Thus if the quantity E, which depends on the nature of the surface of the bulb, be made to vary (if, for example, two bulbs be investigated, one of glass and the other of some metal), then it is found that when both are filled with the same liquid the rates of cooling do not bear a constant ratio for the same excess of temperature. From this we conclude that it is no longer sufficient to multiply the two functions and ϕ by the *same* factor to express the influence of a change in nature of the surface. Analogous results were found for the variables.

Influence of the Nature of the Surface

Excess, $\theta - \theta_0$	Glass, V_1.	Tin Plate, V_2.	V_1/V_2
60	1·39	0·90	1·54
50	1·13	0·73	1·55
40	0·85	0·54	1·57
30	0 62	0 38	1·63
20	0·37	0·21	1·76

These preliminary investigations terminate with a table exhibiting the rate of cooling of water in three differently-shaped bulbs of block-tin. The first was spherical, the second a cylinder of diameter equal to half its height, and the third a cylinder of height equal to half its diameter.

234. Experiments in a Vacuum — Determination of the Function *f*.—In the general expression for the rate of cooling the function ϕ expresses the cooling effect of the gas within the enclosure, and consequently if the enclosure be exhausted so that the thermometer cools in a vacuum, the function ϕ disappears from the expression for V, and we have simply

$$V = Af(E, \theta, \theta - \theta_0).$$

The observations under these conditions will therefore lead to the determination of the function f. It must be remembered however that we know nothing as yet of the properties of any space totally devoid of matter, all that has ever been obtained is a partial vacuum.

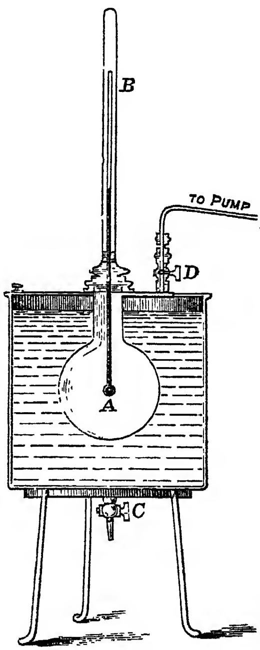


Fig. 124.

The apparatus employed in these experiments consisted of a large copper globe (Fig. 124) about 30 cm. in diameter, and blackened on the inside. This globe formed the cooling chamber or enclosure in which the cooling of the thermometer was observed. It was immersed in a large bath which could be kept at any temperature θ_0 by means of a regulated current of steam. mensions of the thermometer were previously calculated, so

that observations on its cooling could be commenced at about 300° C. The thermometer, when heated to about 350, was placed with its bulb at the centre of the enclosure, which was then rapidly exhausted, and the rate of cooling noted. A small correction was still necessary for the cooling effect of the residue of air left in the cooling chamber, the exhaustion being seldom pushed beyond 3 or 4 mm. The following table contains the results of the experiments, when the chamber was kept at temperatures 0°, 20°, 40°, 60°, 80° respectively :—

VELOCITY OF COOLING IN A VACUUM

Excess of Temperature, $\theta-\theta_0$.	V_1. $\theta_0=0$.	V_2, $\theta_0=20$	V_3, $\theta_0=40$.	V_3, $\theta_0=60$.	V_4, $\theta_0=80$.
° C.					
240	10·69	12·40	14·35		
220	8·81	10·41	11·98	..	.
200	7·40	8·58	10·01	11·64	13·45
180	6·10	7·40	8·20	9·55	11·05
160	4·89	5·67	6·61	7·68	8·95
140	3·88	4·57	5·32	6·14	7·19
120	3·02	3·56	4·15	4·84	5·64
100	2·30	2·74	3·16	3·68	4·29
80	1 74	1·99	2·30	2·73	3·18
60	.	1·40	1·62	1·88	2·17

If the quantities V_1, V_2, etc., at the different temperatures of the enclosure walls be compared, it will be found that the ratios V_2/V_1, V_3/V_2, etc., are approximately the same (1·16) for all values of the excess.

Hence, if we consider the influence of the temperature θ_0 of the chamber, we see that the rates of cooling for the same excess $\theta-\theta_0$, with different values of θ_0, viz. 0°, 20°, 40°, 60°, increasing in arithmetical progression, are such that the ratios V_1/V, V_2/V_1, V_3/V_2, are equal to each other, and we consequently conclude that, for the same excess of temperature, *if the temperature of the chamber be increased in an arithmetical progression, the velocity of cooling will increase in a geometrical progression.*

It follows, therefore, that the velocity of cooling for a given excess can be represented in the form

$$V=Aa^{\theta_0},$$

where A is a function of the excess $\theta-\theta_0$. Denoting this exces for brevity, we have

$$V=a^{\theta_0}\psi(\eta) \quad . \quad . \quad . \quad . \quad .$$

In order to determine the constant a it is only necessary to observe two rates of cooling, V_n and V_{n+1}, corresponding to the same excess, with different values of θ_0. In the above table we have for θ_0 and $\theta_0 + 20°$

$$a^{20} = V_{n+1}/V_n = 1{\cdot}16.$$

Therefore

$$a = (1{\cdot}16)^{\frac{1}{20}} = 1{\cdot}0077.$$

Now by the theory of exchanges the velocity of cooling must be of the form

$$V = f(\theta) - f(\theta_0),$$

or

$$V = f(\eta + \theta_0) - f(\theta_0).$$

Hence by the above experiments we have, using equation (1)

$$f(\eta + \theta_0) - f(\theta_0) = a^{\theta_0}\psi(\eta) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this we obtain, by writing $\theta_0 = 0$ while the excess η remains the same,

$$f(\eta) - f(0) = \psi(\eta) \quad . \quad . \quad . \quad (3)$$

Therefore, by subtracting (3) from (2), we have

$$f(\eta + \theta_0) - f(\theta_0) - f(\eta) + f(0) = \psi(\eta)(a^{\theta_0} - 1).$$

Interchanging η and θ_0 the left-hand side of this equation remains unaltered. Therefore the right-hand member must also remain unaltered in value when η and θ_0 are interchanged, or

$$\psi(\eta)(a^{\theta_0} - 1) = \psi(\theta_0)(a^{\eta} - 1).$$

That is

$$\frac{\psi(\eta)}{a^{\eta} - 1} = \frac{\psi(\theta_0)}{a^{\theta_0} - 1} = k,$$

or

$$\psi(\eta) = k(a^{\eta} - 1),$$

where k is the above function of θ_0.

The general expression for the velocity of cooling becomes therefore

$$V = ka^{\theta_0}(a^{\eta} - 1) = k(a^{\theta} - a^{\theta_0}).$$

If in the foregoing table the observed values of V be compared with their corresponding values calculated by this formula, the close agreement exhibited will show that the equation is capable of representing the facts with considerable accuracy. On the whole, however, it cannot be regarded as having any sound theoretical basis, but must be looked upon merely as an empirical formula of wider range [illegible]n Newton's. Its simplicity might lead us to fancy that it could be [illegible]ined theoretically, but until we possess more information about [illegible]mechanism of emission we have no ground on which to base a

To terminate their vacuum experiments, Dulong and Petit observed the effect of varying the surface of the thermometer bulb. They found that the rate of cooling when the surface was naked differed from that when it was coated with silver-foil or any other substance. The quantity a was found, however, to remain unaltered, so that it does not depend on the surface emissivity, or on the mass or nature of the liquid, and the coefficient k alone was found to vary with the nature of the surface.

235. Experiments in a Closed Chamber containing a Gas.—A series of experiments on the cooling of a thermometer in a vacuum having been completed, a further series on the cooling of the same thermometer in the same chamber when occupied by a gas will furnish the data necessary to the calculation of the cooling influence of the gas. In this case we have already written the general expression for the velocity of cooling in the form

$$V = Af(E, \theta, \theta - \theta_0) + A\phi(E, \theta, \theta - \theta_0, p, G),$$

and since the first term of the left-hand member of this equation represents the cooling in a vacuum, it may be replaced by the quantity $k(a^\theta - a^{\theta_0})$, and if the velocity V be observed we have then for ϕ

$$A\phi = V - k(a^\theta - a^{\theta_0}).$$

The first point investigated by Dulong and Petit[1] was the influence of the nature of the surface of the bulb on the cooling function ϕ of the gas. Having determined the rate of cooling in a vacuum when the bulb was naked, and also when it was silvered, they repeated the same experiments in air and other gases, and the results showed that the cooling power of the gas did not depend on the nature of the surface; or, in other words, the coefficient E of the surface does not enter into the function ϕ. This is shown by the following table:—

INFLUENCE OF THE NATURE OF THE SURFACE

Excess of Temperature, $\theta - \theta_0$.	Difference of Velocities of Cooling in Vacuum and in Air at 20° and 720 mm.	
	Bulb naked.	Bulb silvered.
°		
200	5·48	5·43
180	4·75	4·79
160	4·17	4·19
140	3·51	3·52
120	2·90	2·88
100	2·27	2·32

[1] *Ann. de Chimie et de Phys.*, 2e, tom. vii. p. 337, 1817.

Thus the cooling effect of the gas appears to be absolutely independent of the emissivity of the surface. This result appears to have been first remarked in a general way by Sir J. Leslie, and is a fact of great importance in the study of the conductivity of gases.

The influence of the temperature θ_0 of the enclosure on the cooling power of the gas was next examined. The pressure being kept constantly at 720 mm., the temperature of the enclosure was brought successively to 20°, 40°, 60°, 80°, with the result that the cooling effect of the air for a given excess was found to be the same for all values of θ_0. This is exhibited in the following table :—

INFLUENCE OF THE TEMPERATURE OF THE ENCLOSURE

Excess, $\theta - \theta_0$.	Cooling Effect of Air at 720 mm.			
	$\theta_0=20°$.	$\theta_0=40°$.	$\theta_0=60°$.	$\theta_0=80°$.
°				
200	5·48	5·46	...	.
180	4·75	4·70	4·79	.
160	4·17	4·16	4·20	4·13
140	3·51	3·55	3·55	3·49
120	2·90	2·93	2·94	2·88
100	2·27	2·28	2·24	2·25
80	1·77	1·73	1·71	1·78
60	1·23	1·19	1·18	1·20

As a result of these experiments, it appears that the cooling function ϕ depends only on the excess of temperature $\theta - \theta_0 = \eta$, and in a manner yet to be determined on the pressure p and nature G of the gas, so that it may now be written in the form $\phi(\eta, p, G)$. In order to determine the influence of variations of pressure, Dulong and Petit experimented in air at a series of pressures, 720, 360, 180, 90 mm., decreasing in a geometrical progression. The results of these experiments are contained in the following table, and they show that for any given excess the cooling effect of a given gas increases in a geometrical progression of ratio 1·366 when the pressure increases in a geometrical progression of ratio 2 :—

[TABLE

INFLUENCE OF THE PRESSURE OF THE GAS

Excess, $\theta-\theta_0$.	Cooling Power of Air.						
	ϖ_1, $p=720$.	$\frac{\varpi_1}{\varpi_2}$.	ϖ_2, $p=360$.	$\frac{\varpi_2}{\varpi_3}$.	ϖ_3, $p=180$.	$\frac{\varpi_3}{\varpi_4}$.	ϖ_4. $p=90$.
°							
200	5·48	1·37	4·01	1·36	2·95	1·34	2·20
180	4·75	1·35	3·52	1·35	2·61	1·37	1·90
160	4·17	1·37	3·03	1·37	2·21	1·36	1·62
140	3·51	1·34	2·62	1·37	1·91	1·36	1·40
120	2·90	1·37	2·12	1·35	1·57	1·37	1·15
100	2·27	1·34	1·69	1·37	1·23	1·36	0·90
80	1·77	1·37	1·29	1·34	0·96	1·37	0·70
60	1·23	1·36	0·90	1·37	0·65	1·35	0·48

It thus appears that when the pressure p is related to the pressure p' by the equation

$$p=2^n p' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The corresponding cooling powers ϖ and ϖ' of the air are related by the equation

$$\varpi=(1\cdot366)^n\varpi' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

From (1) and (2) it follows at once that

$$\frac{\log(\varpi/\varpi')}{\log(p/p')}=\frac{\log(1\cdot366)}{\log 2}=0\cdot45,$$

and therefore

$$\frac{\varpi}{p^{0\cdot45}}=\frac{\varpi'}{p'^{0\cdot45}},$$

or denoting the value of this ratio by μ, we have for the general relation between the cooling power of air and the pressure

$$\varpi=\mu p^{0\cdot45}$$

The equation connecting the cooling power and pressure of any gas may therefore be written in the form

$$\varpi=\mu p^c,$$

where μ is a function of the excess of temperature and of the nature of the gas. The index c is different for the different gases examined by Dulong and Petit, as follows :—

Air	$c=0\cdot45$	Hydrogen	$c=0\cdot$
Carbonic acid . .	$c=0\cdot517$	Olefiant gas	$c=0$

The influence of the excess of temperature still remains t examined. For this purpose the foregoing table suffices. F

comparison of the cooling powers corresponding to different values of the excess $\theta - \theta_0$, but the same value of p, it appears that as the excess increases in a geometrical progression of ratio 2, the cooling power increases in a geometrical progression of ratio 2·33, and hence, if

$$\eta = 2^n \eta',$$

we have for a constant pressure

$$\varpi = (2·33)^n \varpi'.$$

Therefore

$$\frac{\log (\varpi/\varpi')}{\log (\eta/\eta')} = \frac{\log (2·33)}{\log 2} = 1·233.$$

and consequently

$$\frac{\varpi}{\eta^{1·233}} = \frac{\varpi'}{\eta'^{1·233}}.$$

Denoting the common value of each of these ratios by m, we have for the relation between the cooling power of air and the excess of temperature η the equation

$$\varpi = m\eta^{1·233}.$$

The experiments further prove that while the coefficient m is different for different gases, the index 1·233 remains the same for all, so that the complete expression for the cooling power of any gas may be written in the form

$$\varpi = mp^c(\theta - \theta_0)^{1·233},$$

and hence the whole velocity of cooling in a gas is determined by the equation

$$V = k(a - a^{\theta_0}) + mp^c(\theta - \theta_0)^{1·233}.$$

Such is the general expression to which the experiments of Dulong and Petit have led. The first term relates to the radiation alone, while the second deals with the cooling effect of the ambient gas. The whole, however, must be regarded simply as an empirical formula founded on one of the most elaborate series of experiments ever conducted.

236. Experiments of De la Provostaye and Desains.—The range of applicability of the formula of Dulong and Petit has been made the subject of a careful investigation by MM. De la Provostaye and Desains.[1] The result of the new researches proved that the formula could be applied only within a limited range, like all other empirical [redacted]ulæ, in the neighbourhood of the experiments from which the ...s constants happened to be determined. Thus the quantity k ...und to be only approximately constant. Its value varied little

[1] ... la Provostaye et P. Desains, *Ann. de Ch. et de Phys.*, 3e, t. xvi. p. 337, 1846.

with a naked-bulbed thermometer, but with a silvered bulb it changed from 0·0087 at 150° C. to 0·0109 at 63° C. The constant m was also found to depend to some extent on the emissivity E, being greater for a metallic surface than for the naked glass. But perhaps the most important result of the investigation was that the cooling power ϖ of the gas was found not to be proportional to a power of the pressure (p^c) when the pressure was feeble. The experiments appear to show that as the pressure diminished from 760 mm., the value of ϖ decreased at first, and then remained constant from a value p_1 to a value p_2 of the pressure, after which it augmented with reduction of pressure. These limiting pressures p_1 and p_2 were further found to be more elevated and more widely separated the smaller the dimensions of the enclosure, as shown by the following table :—

Enclosure	p_1.	p_2.
	mm	mm
Sphere, 24 cm. diameter . .	4	2·8
,, 15 cm. ,, . .	20	4
Cylinder 15 c. high and 6 c. diameter.	70	15

This behaviour is to be attributed to the effect of the diminution of pressure and of the smallness of the chamber on the convection currents. Under these circumstances the cooling effect due to convection will be almost entirely eliminated, and the cooling due to the gas takes place entirely by molecular convection.

237. Stefan's Law.—From a careful examination of the results of Dulong and Petit's experiments, M. Stefan [1] was led to the conclusion that the total radiation emitted by any body is proportional to the fourth power of the absolute temperature of the body. This law does not mean that the rate of cooling of the body is proportional to the fourth power of the absolute temperature, but that the function $f(\theta)$, which represents the emission of the body on p. 445, is equal to the fourth power of the absolute temperature multiplied by some constant depending on the nature of the body. Thus, denoting the absolute temperature by τ we have $\tau = 273 + \theta$ (Art. 290), where θ is the temperature centigrade, and $f(\theta) = A\tau^4$. Hence if a body at θ° C. cools in an enclosure at 0° C., the rate of cooling will be determined by the formula

$$\iota = A\{(273+\theta)^4 - (273)^4\}.$$

[1] Stefan, *Sitzungsberichte d. K. Akademie d. Wissenschaften in Wien*, v. 1879 ; and *Journal de Physique*, tom. x. p. 317, 1881.

In support of this law we have the following table, the first two columns of which are taken from Dulong and Petit's results (p. 452). The third column is calculated by the above formula (the constant A being suitably chosen), and it will be observed that the differences are not greater than those which exist between the observations and calculations of Dulong and Petit.

θ.	Rate of Cooling	Calculated.	Difference
°C			
80	1·74	1·66	−0·08
100	2·30	2·30	0
120	3·02	3·05	+0·03
140	3·88	3·92	+0·04
160	4·89	4·93	+0·04
180	6·10	6·09	−0·01
200	7·40	7·42	+0·02
220	8·81	8·92	+0·11
240	10·69	10·62	−0·07

Again, taking the difference of the rates of cooling of the same thermometer when naked and silvered respectively (the influence of the conductivity of the air disappearing in this difference), MM. Provostaye and Desains found

Temperature.	Rate of Cooling.		Difference.
	Naked.	Silvered.	
°C.			
75·10	0·05675	0·02035	0·03640
96·86	0·08318	0·02876	0·05442
108·60	0·09966	0·03333	0·06633
121·88	0·11934	0·03859	0·08075
136·58	0·14360	0·04479	0·09881

Dividing the numbers in the last column by the difference of the fourth powers of the corresponding temperatures of the thermometer and enclosure (0° C.), we obtain the numbers

4648, 4588, 4621, 4624, 4641,

which are very fairly equal. Dividing the fourth column numbers by ...1, according to the law of Dulong and Petit we obtain the ...ers

6212, 6236, 6327, 6374, 6432,

...e not nearly so constant.

It has been shown quite recently by B. Galitzine[1] that Stefan's law follows theoretically from the principles of thermodynamics and the electromagnetic theory of light, and the same result was previously deduced by Boltzmann.

Emissivity in Absolute Measure

238. M'Farlane's Experiments.—The first trustworthy experiments, yielding emissivities in absolute measure, were those made by Dr. Donald M'Farlane[2] in Glasgow, under the direction of Lord Kelvin. The method adopted consisted in observing the cooling of a copper sphere about 4 cm. in diameter. This sphere was suspended inside a double-walled tin-plate vessel, which had its interior coated with lamp-black and the space between its walls filled with water at the temperature of the atmosphere. Its temperature was taken by means of a thermoelectric couple, one junction of which was situated at the centre of the sphere, and the other junction was in metallic contact with the outside of the tin-plate vessel, the circuit being completed through the coil of a sensitive mirror galvanometer. One junction was thus kept at a constant temperature of about 14° C., while the other had the gradually-diminishing temperature of the centre of the sphere.

In making an experiment the copper ball was heated in the flame of a spirit-lamp till its temperature was considerably above that required to throw the spot of light off the galvanometer scale. It was then placed in position within the tin-plate water jacket, and as soon as the spot of light came within range, the deflections from the zero position were noted at intervals of one minute until the change of deflection was reduced to about two scale divisions per minute.

Two series of experiments were made in this way. In the first the surface of the ball was bright, and in the second it was coated with a thin covering of soot from a lamp flame, and in both the air was kept moist by a saucer of water placed inside the enclosure.

The following table gives the results for every fifth degree within the limits of the experiments:—[3]

[1] Galitzine, *Wied. Annalen*, vol. xlvii. pp. 479-495, Nov. 1892. Translated *Phil. Mag.*, Feb. 1893.

[2] D. M'Farlane, *Proc. Roy. Soc.*, vol. xx. p. 90, 1871.

[3] Professor Tait has published results obtained by Mr. J. P. Nicol on the heat from polished and blackened copper at three different pressures—76[illegible] 10 mm. of mercury (*Proc. Roy. Soc.*, Edinb., 1869-70), and the results experiments agree with those given in the table (p. 461) as closely as expected.

Difference of Temperature.	Heat emitted per Second, per Degree Difference of Temperature, per Square Centimetre in Water-gramme Units.		
	Polished Surface.	Blackened Surface.	Ratio.
c			
5	·000178	·000252	·707
10	186	266	·699
15	193	279	·692
20	201	289	·695
25	207	298	·694
30	212	306	·693
35	217	313	·693
40	220	319	·693
45	223	323	·690
50	225	326	·690
55	226	328	·690
60	226	328	·690

The heat emitted per second was calculated by the formula $Q = a + b\theta + c\theta^2$, where θ is the difference of temperature.

The couple was standardised by tying its ends to the bulbs of two previously compared thermometers, placed in two vessels of water, one at the temperature of the air and the other heated by small additions of hot water.

239. Bottomley's Experiments.—More recently the same subject has been attacked by Dr. J. T. Bottomley.[1] In this investigation the radiating body was a platinum wire stretched inside a long copper tube which was blackened on the inside and kept cool by a water jacket. The wire was heated by an electric current, and its surface might be bright and polished or might be coated with lamp-black, platinum-black, oxide of copper, or some other material.

Two methods of estimating the electric energy were employed. One consisted in measuring the current and the difference of potential between two chosen points on the radiating wire; the other consisted in measuring the current and determining simultaneously the resistance of the wire by means of a specially-designed Wheatstone's bridge. The resistance when known gives the temperature of the wire. The energy supplied to the wire by the electric current is lost through radiation and by conduction at its ends, but the latter source of loss is negligible, and when the dimensions of the wire are known the area of its surface is known, and the rate of loss of heat per unit area becomes determined at any temperature.

n order to obtain data for the elimination of the cooling effect of ·, the copper tube was connected with a five-fall Sprengel pump,

[1] J. T. Bottomley, *Phil. Trans.*, 1887, p. 429.

so that the air pressure could be reduced, and in the extreme vacuum it was measured by a M'Leod's gauge.

A long and very complete series of determinations was made in this manner at various constant pressures and at different gradually increasing temperatures. Several series of observations were also taken at constant temperature while the pressure was gradually diminished. This mode of procedure proved by far the most appropriate to the purpose in hand, and required the use of a special current-meter. On reducing the pressure it was found that a point was reached at which further exhaustion did not affect the emission. In this way a condition seems to be gradually reached in which the radiation is independent of everything removable by a Sprengel pump.

The temperature of the envelope being 15° C., the value of the emission per square centimetre of a bright platinum wire was in water-gramme-centigrade units—

At 408° C.	$378 \cdot 8 \times 10^{-4}$.
,, 505° C . . .	$726 \cdot 1 \times 10^{-4}$.

Dr. Bottomley considers that these experiments do not support the fourth power law of Stefan, and that a similar series of experiments by Schleiermacher[1] contradicts this law in the same manner.

Evans's experiments.

Some interesting results obtained by Mr. Evans[2] as to the energy necessary to maintain a given candle-power in an incandescent lamp were confirmed during this investigation. The object of Evans's experiments was to compare the radiation of the carbon filaments of incandescent lamps having a bright polished surface with that from those having a dull surface like lamp-black, and he was led to an important practical conclusion as to the superior light-giving efficiency of the bright-looking filaments. If it be allowed that the temperature of a carbon filament can be measured by its resistance (this diminishing as the temperature increases), it follows from Evans's results that the temperature to which a filament must be raised, in order that it may furnish light of a definite candle-power, is higher when the surface is dull than when it is in the brilliant metallic-looking state. This result was so unexpected that Bottomley put it to the test of direct experiment. The result confirmed the conclusions derived from the experiments of Evans, and showed that the temperature which produces red-heat (for example) is very much higher when the surface of the heated body is dull than when it is bright and polished. T in the case of two platinum wires contained in vacuum tubes, one

[1] Schleiermacher, *Wied. Ann.*, vol. xxvi. p. 287, 1885.

[2] M. Evans, *Proc. Roy. Soc.*, vol. xl. p. 207, 1886.

being bright and the other dulled with a thin film of smoke, when at the same dull red-heat the glass tube which contained the bright wire was not unpleasantly warm to the hand, while that containing the other wire was hot enough to blister the skin. The ratio of the resistances of the wires in this state was as 130 : 93, so that their difference of temperature must have been considerable.[1]

[1] Professor Crookes (*Proc. Roy. Soc.*, vol. xxi. p. 239, 1881) has given a valuable comparative determination of the loss of heat from the same surface (the bulb of a mercury-in-glass thermometer) at different pressures, varying from one atmosphere down to two-millionths of an atmosphere.

SECTION III

DIATHERMANCY

DIATHERMANCY OF SOLIDS AND LIQUIDS

240. Melloni's Experiments.—Substances like glass which transmit light are said to be transparent, and in a similar manner those which permit radiant heat to pass through them are said to be diathermanous. At first sight it might be surmised that those bodies which most freely transmit light also most copiously transmit the non-luminous rays, such as the radiation from hot water pipes, and that substances which are opaque to light are also opaque to radiant heat; but a little consideration will prepare any one possessing a knowledge of the fundamental principles of the wave theory to expect that different substances may behave very differently in their transmission of non-luminous radiation. The marked difference of behaviour in the transmission of light is detected at once by the eye, and may be more closely studied by an examination of the spectrum of the transmitted light. Thus blue glass and sulphate of copper transmit only the blue end of the spectrum, and red glass intercepts this end and transmits only the red; and the striking feature of these cases is the powerful effect of an almost infinitesimal amount of colouring matter on the transmission of light.

A solution of permanganate of potash intercepts the middle portion of the spectrum and transmits both ends, the mixture of red and blue giving rise to the gorgeous colour of the solution. Various substances are thus proved to possess what is termed selective absorption as regards the waves of light, singling out certain waves for destruction while they permit others to pass. Hence if the non-luminous radiation, like the luminous, be a wave motion in the ether, we are prepared to find that transparency to light does not necessarily imply transparency to radiant heat, and that a substance which is opaque to light may freely transmit non-luminous radiation, and further, that stance which is transparent to the radiation from one source practically opaque to that of another.

When light and heat were considered to be essentially different, however, this view was not so easily entertained. Those who espoused the caloric theory found it very difficult to admit that heat could be transmitted through any substance in the same manner as they conceived light to be. All cases in which heat appeared to be so transmitted were explained by supposing that the heat was first absorbed by the substance, and afterwards radiated by it when it became hot. That heat can be transmitted almost instantaneously like light seems to have been discordant with the ideas of the calorists, and the point was combated by them for some time after the conclusive experiments of De la Roche and Melloni.

The transmission of heat and the property of selective absorption by bodies for the dark rays was first established by De la Roche, who concluded from this that radiant heat consists of a mixture of different rays, or, as we should now say, a multitude of waves of different lengths, just as white light is a mixture of different waves or differently coloured rays.

The work of De la Roche was subsequently confirmed by the elaborate researches of Melloni[1] with the thermopile. The method of analysis adopted may be briefly described as follows. The source of heat was placed at one side of a screen provided with an aperture, and the thermopile was placed at the other, so that the radiation, after passing through the aperture, fell upon it either unobstructed or after passing through a thin plate of the material under examination. In this manner Melloni found that rock-salt was exceedingly diathermanous, transmitting over 90 per cent of the incident radiation, whereas plates of alum and pure water of the same thickness scarcely transmitted the tenth part of the radiation from a lamp flame, and an inappreciable amount of the radiation from low temperature sources, such as a blackened copper ball heated to 390° C., or a Leslie's cube.[2]

[1] Melloni, *Ann. de Chimie et de Physique*, 2e, tom. liii. p. 5, 1833, and tom. lv.

[2] Rock-salt transmits a very large percentage of the radiation from all the sources, whereas alum transmits, according to Melloni, only the luminous rays (this, however, is not quite correct). Hence if, as Melloni supposed, the rock-salt transmits all the radiation, the difference between the quantities transmitted by a plate of rock-salt and a plate of alum should give the value of the obscure radiation as compared with the luminous. Tested in this way Melloni found the following proportions for the three sources employed :—

Source.	Luminous.	Obscure.
Oil flame	10	90
Incandescent platinum	2	98
Flame of spirit-lamp	1	99

The results of experiments with four different sources of heat are contained in the following table, which exhibits not only the difference of diathermancy of different substances for the radiation from the same source, but also the difference of behaviour of the same substance towards the radiation from different sources. The numbers represent the percentages of the incident radiation transmitted by the various substances. Four sources of heat were employed: (1) a Locatelli lamp without a glass chimney; (2) a platinum spiral heated to incandescence in the flame of a spirit-lamp; (3) a copper plate heated to nearly 400° C. by a spirit-lamp; (4) a thin copper vessel blackened on the outside and filled with boiling water.

Thickness 2·6 mm	Locatelli Lamp.	Incandescent Platinum	Blackened Copper heated to 390°.	Blackened Copper heated to 100°.
Rock-salt (clear) . .	92	92	92	92
Fluate of lime (clear) . .	78	69	42	33
Rock-salt (dull) . .	65	65	65	65
Beryl (greenish-yellow) . .	54	23	13	0
Fluate of lime (greenish) .	46	38	24	20
Iceland spar	39	28	6	0
,, ,, . .	38	28	5	0
Mirror glass	39	24	6	0
,, ,, ...	38	26	5	0
Rock-crystal (clear) .	38	28	6	0
,, ,, (smoky) . .	37	28	6	0
Acid chromate of potash .	34	28	15	0
White topaz . . .	33	24	4	0
Carbonate of lead . . .	32	23	4	0
Sulphate of barytes (pure) .	24	18	3	0
White agate	23	11	2	0
Adularia felspar . .	23	19	6	0
Amethyst (violet)	21	9	2	0
Amber (artificial)	21	5	0	0
Emerald . .	19	13	2	0
Agate (yellow) . .	19	12	2	0
Borate of soda . . .	18	12	8	0
Green tourmaline . .	18	16	3	0
Cow horn	18	4	0	0
Common gum . .	18	3	0	0
Sulphate of barytes (dull)	17	11	3	0
Sulphate of lime .	14	5	0	0
Sardoin . .	14	7	2	0
Citric acid . .	11	2	0	0
Amber (natural)	11	5	0	0
Alum . .	9	2	0	0
Glue (strong)	9	2	0	0
Mother-of-pearl . .	9	0	0	0
Green fluate of lime .	8	6	4	3
Melted sugar .	7	0	0	
Ice (very pure) . . .	6	0	0	

This table shows how different substances differ in diatl

and it also shows that, with a single exception, the diathermancy of each substance varies with the nature of the source of heat. Rock-salt alone appears to be equally transparent to the radiation from all sources. Melloni supposed this substance to be perfectly transparent to all kinds of radiation, and that the 8 per cent deficit in the foregoing table arose from reflection at the surfaces of the plate and not from absorption in the interior. More recent experiments, however, by MM. Provostaye and Desains have proved that rock-salt does exhibit selective absorption, and as already mentioned (p. 439), Balfour Stewart demonstrated that it is particularly opaque to the radiation from a heated piece of the same substance.

In the case of liquids the diathermancy was examined by enclosing them in a glass cell with parallel faces. The source of heat was an Argand-lamp furnished with a glass chimney, so that in considering the results of the following table it must be remembered that the diathermancy of the liquid is for the radiation of the lamp in question after passing through glass:—

Liquids, thickness 9·21 mm.	Rays transmitted.
No screen	100
Mirror glass (same thickness as liquid)	53
Carburet of sulphur (colourless)	63
Chloride of sulphur (brownish-red)	63
Protochloride of phosphorus (colourless)	62
Hydrocarburet of chlorine	37
Nut oil (yellow)	31
Essence of turpentine (colourless)	31
Essence of rosemary ,,	30
Oil of colza (yellow)	30
Oil of olives (greenish-yellow)	30
Naphtha (natural, light brown-yellow)	28
Balsam of copaiba (brown-yellow)	26
Essence of lavender (colourless)	26
Naphtha (rectified, colourless)	26
Sulphuric ether (colourless)	21
Pure sulphuric acid (colourless)	17
Nordhausen sulphuric acid (brown)	17
Hydrate of ammonia (colourless)	15
Nitric acid (pure and colourless)	15
Alcohol (absolute and colourless)	15
Hydrate of potassium (colourless)	13
Acetic acid (rectified, colourless)	12
Pyroligneous acid (brownish)	12
Sugared water (colourless)	12
Alum water ,,	12
Salt water ,,	12
White of eggs (slightly yellowish)	11
Distilled water	11

This table shows that pure water is exceedingly opaque to radiant heat, and that the solution of a salt in it increases rather than diminishes its diathermancy. The position of a solution of alum is worthy of remark in this respect, for it seems to have been very generally supposed that this solution is practically opaque to non-luminous heat. The above table shows that Melloni found it more diathermanous than pure water, and this conclusion has been verified by Mr. Shelford Bidwell.[1] The ordinary supposition may perhaps have arisen from the fact that a plate of alum is highly opaque to thermal radiation (but not so much so as sugar-candy or ice), and it may have been inferred that its solution would also be highly opaque.

Alum cell.

Sifting.

The diathermancy of any body to radiation which has already passed through another was also examined by Melloni. The results are contained in the following table. It appears that any substance is particularly transparent to radiation which has already been sifted by a plate of that substance. Thus a plate of alum which only transmitted 9 per cent of the heat from a naked lamp transmitted 90 per cent of that which had already passed a plate of this material. The same remark applies to the other substances, so that all are capable of sifting heat in such a manner that a second plate will transmit a large portion of the heat which has already passed through a plate of the same material. This of course is what we should expect theoretically, for when the radiation passes through a plate of any substance the emergent beam consists chiefly of those waves which the substance freely transmits, and this will be almost entirely transmitted by a second plate of the same substance.

Examples of athermanous combinations are also contained in the table, just as red and green glass together make a combination opaque to light. Thus rays which have passed through alum are very feebly transmitted by black mica or black glass.

[1] *Brit. Ass. Report*, p. 309, 1886.

Plates not specially indicated were 2·6 mm	Rays from Lamp.	Rays from Alum, thickness 2·6 mm.	Rays from Sulphate of Lime, thickness 2·6 mm.	Rays from Chromate of Potash, 2·6 mm	Rays from Green Glass, 1·85 mm.	Rays from Black Glass, 1·85 mm.
Rock-salt	92	92	92	92	92	92
Fluate of lime	78	90	91	88	90	91
Beryl	54	80	91	66	70	57
Iceland spar	39	91	89	56	59	55
Glass (0·5 mm.)	54	90	85	68	87	80
,, (0·8)	34	90	82	47	56	45
Rock-crystal	38	91	85	52	78	54
Chromate of potash	34	57	53	71	28	24
Sulphate of barytes	24	36	47	25	60	57
White agate	23	70	78	30	43	17
Adularia felspar	23	23	58	43	50	23
Yellow amber	21	65	61	20	13	8
Black opaque mica (0·9)	20	0·4	12	16	38	43
Yellow agate	19	57	64	24	35	14
Emerald	19	60	57	26	20	21
Borate of soda	18	23	33	23	30	24
Green tourmaline	18	1	10	14	24	30
Common gum	18	61	52	12	6	4
Sulphate of lime	14	59	54	22	9	15
,, ,, thick (12 mm.)	10	56	45	17	5	0·4
Carbonate of ammonia	12	44	34	11	6	5
Citric acid	11	88	52	16	3	2
Tartrate of potash and soda	11	85	60	15	2	1
Alum	9	90	47	15	0·2	0·3
Coloured Glasses, 1·85 mm. thick.						
White glass	40	90	83	50	67	55
Violet	34	76	72	42	56	47
Red	33	74	69	41	54	45
Orange	29	65	58	36	48	39
Apple-green	25	3	20	22	55	50
Mineral-green	23	1	15	19	52	58
Yellow	22	49	46	27	35	30
Blue	21	47	42	26	34	29
Black (opaque)	16	0·5	18	11	42	52
Indigo	12	27	26	14	20	17

241. Influence of the Temperature of the Source.—It was for some time supposed that the transmissibility of heat through diathermic substances augmented with the temperature of the source. Knoblauch[1] was the first to prove that this is not the case, but that the passage of radiant heat through any substance is determined alone the nature of the substance. He showed in these researches that heat emitted by an alcohol flame was more absorbed by certain ances than the heat emitted by a platinum wire placed in the

[1] Knoblauch, *Pogg. Ann.*, 1847; and Taylor's *Scientific Memoirs*.

flame, and he argued that the temperature of the flame cannot be lower than that of the spiral. Thus a plate of transparent glass placed between the incandescent platinum spiral and the thermopile transmitted a greater percentage of the radiation than when the source of heat was the flame alone without the spiral. This showed that the heat from the spiral, or source of lower temperature, was best transmitted, and this result was afterwards verified by Melloni.

Glass. Transparent glass allows the luminous or shorter waves to pass freely through it, but it is highly opaque to the longer, or ultra red-waves, that is to the obscure or non-luminous radiation. Reference to the foregoing tables shows that a plate of glass of the kind employed by Melloni, and only one-tenth of an inch thick, intercepts all the radiation from a source at 100° C., and transmits only 6 per cent of the heat emitted by a source at 400° C. It is for this reason that a glass plate is often used as a fire-screen. Now the radiation from the flame of a spirit-lamp is nearly all non-luminous, but when a platinum spiral is plunged in the flame the luminosity is largely increased. The spiral becomes incandescent, absorbing the non-luminous waves of the flame, and emitting in return a copious supply of the shorter luminous waves. In this manner the percentage of waves which are easily transmitted by glass, is increased, and the presence of the spiral augments the transmissibility of the radiation. Thus Melloni found that a glass plate transmitted 41·2 per cent of the radiation from the flame alone, and 52·8 per cent of that from the flame and spiral. A plate of selenite transmitted in the same way 4·4 per cent from the flame, and 19·5 from the spiral.

In the case of substances which are opaque to the waves of higher refrangibility, the presence of the spiral would be expected to produce an opposite effect and reduce the transmissibility, for in this case the action of the spiral is to increase that portion of the radiation which is not transmitted by the substance. This was also verified by Melloni. Thus for black glass he found a transmission of 52·6 per cent from the flame, and only 42·8 from the spiral, and for black mica a transmission of 62·8 from the flame, and 52·5 from the spiral.

Diathermancy of Gases and Vapours

242. Tyndall's Experiments.—The first successful experiments on the transmission of radiant heat through gases were made Professor Tyndall at the Royal Institution in 1859. Previous to date no experimenter had been able to detect any absorption of ra heat by gaseous matter, and it was generally supposed that mat

the gaseous state transmitted perfectly all kinds of radiation. In approaching this investigation, either of two distinct methods of attack may be adopted: (1) the thermopile and the source of heat may be both placed in the chamber containing the gas under consideration; or (2) either or both may be situated outside the space enclosing the gas. The first method has been employed by Magnus and others, and will be considered later on. It is subject, as Tyndall[1] pointed out, to errors arising from convection currents and conduction of heat, and for this reason Tyndall adopted the second mode of experiment.

In making a preliminary experiment by this method, a tube about 4 feet long and 3 inches in diameter was fitted air-tight with rock-salt plates at the ends and furnished with two stopcocks, so that it could be exhausted or filled with air or any other gas. The source of heat was placed opposite one end, and the thermopile faced the other, so that the radiation, after traversing the tube, fell upon it and produced a deflection of the galvanometer needle. The tube was first exhausted and the deflection of the galvanometer noted when the radiation fell upon the pile after traversing the empty space. Pure dry air was then admitted, and the deflection was found to remain unaltered, so that the radiation seemed to be transmitted as freely through the air as through a vacuum. The first inference is that either air does not absorb radiant heat at all, or else to such a small extent that this mode of experiment fails to detect it. Or it might happen that rock-salt and air absorb the same kind of rays, and that the radiation, after passing through the first plate of salt, is so sifted that no waves of the particular kind absorbed by air remain.

Rock-salt was chosen to close the ends of the tube, because it is by far the most diathermanous substance we know of. It is not particularly necessary to have a transparent substance, for gases, we know, freely transmit the luminous waves, and if they possess

[1] Previous to the work of Tyndall, no doubt, many experimenters had investigated the action of air upon radiant heat; otherwise the conviction that air perfectly transmitted radiant heat could not have become so universal, but that all other gases were supposed to behave in a like manner proves that experiments on them could scarcely have been seriously attempted.

Dr. Franz of Berlin (*Pogg. Ann.*, vol. xciv. p. 342) with a sensitive thermopile had discovered a supposed absorption by dry air in a 3-foot tube of 3·54 per cent; but this was attributed by Tyndall to the fact that Franz employed glass plates to close the ends of the tube, and as glass largely absorbs the non-luminous radiation, plates soon become warm and radiate heat to the pile. In this situation of , when the cool gas is admitted into the tube it rapidly lowers the temperature radiating glass plates both by conduction and convection, so that the total to the pile is reduced just as if the gas exercised a true absorption of the heat.

any marked absorbing power, it must be for waves below the red. The essential thing then is to stop the ends of the tube with plates of some substance which freely transmits the longer waves below the red, and rock-salt is the best yet found for this purpose.

Tyndall, however, did not rest satisfied with this negative reply to his inquiry. He was fully convinced that air probably did absorb some of the radiant heat, but such a small fraction that the apparatus failed to detect it. He consequently exercised his ingenuity to render the apparatus more and more delicate, so that even the very feeblest absorption might be fully placed in evidence. This required a strong source of heat, so that a small fraction of it might not be infinitesimal, and it also required the galvanometer needle to be kept in the most sensitive position. A strong source of heat produces a large deflection of the needle, and in this part of the scale the instrument is not very sensitive to small changes of heat. The problem to be solved then was to work with small deflections and a strong source.

This difficulty was overcome by Tyndall in the following manner. The indications of the thermopile depend not so much on the temperature of either face as on their difference of temperature, and when the two faces are brought to the same temperature the deflection of the galvanometer is reduced to zero. The solution of the difficulty is now obvious. For if a strong beam of radiant heat be employed, which, falling on one face of the pile, produces a large deflection of the needle, then by bringing up a second source of heat opposite the other face of the pile, the action of the first source may be counterbalanced by the second, and the galvanometer deflection may be reduced to zero if desired. Let us now suppose that this has been effected, and that the needle stands at zero and in equilibrium under the joint action of the two sources of heat; and let us further suppose that the experimental tube already described has been exhausted and placed in the path of one of the beams of heat, so that the beam of radiant heat, falling upon one of the faces of the pile, passes through the empty tube. Now let us suppose air or any other gas to be introduced into the tube. Then if this gas absorbs any small fraction of the heat, the previous equilibrium will be broken and the needle will move to a new position of rest. The deflection of the needle will be, within certain limits, proportional to the quantity of heat absorbed, and this for a substance of given absorbing power will be proportional to the intensity of the beam passing through the tube. Hence the stronger the beam of radiant employed the greater the ultimate indication of the galvanomete by the foregoing device it is rendered possible to use a b any strength desired. The preliminary difficulty being thus ov

Tyndall again approached the inquiry, and with marked success, as will appear from what follows.

The type of apparatus finally adopted is sketched in Fig. 125. The experimental tube SS′ was a hollow brass cylinder, polished within, and closed air-tight at the ends S and S′ with plates of rock-salt. The length of this tube was about 4 feet, and the source of heat C was a cube of cast copper filled with water, which was kept boiling by a lamp. The cube C was not isolated but brazed to a short cylinder F of the same diameter as the experimental cylinder, and capable of being connected air-tight with the latter at S. Thus between the source of heat and the experimental tube there was a front chamber F which could be exhausted, so that the radiation from C might enter the experimental tube unsifted by air. In order to avoid conduction of heat from C to the rock-salt plate at S, the front chamber F passed

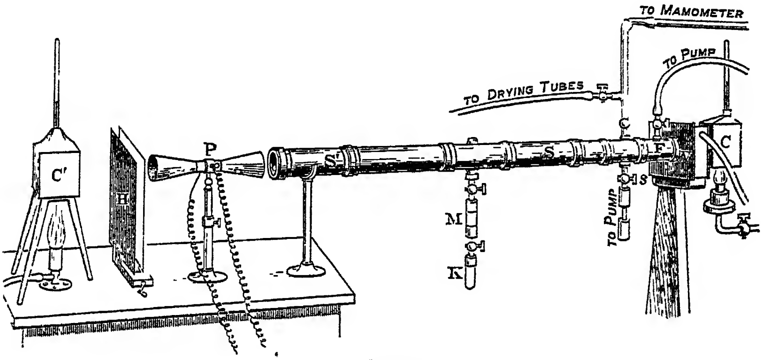


Fig. 125.

through a vessel V, in which a stream of cold water continually circulated. The experimental tube and the front chamber F were connected, independently, with the air pump, so that either of them might be filled or exhausted without interfering with the other. The thermopile P was furnished with a conical reflector at each end, and the compensating cube C′ was used to neutralise the radiation from C. An adjusting screen H, capable of a very fine motion to and fro, was employed to bring about exact compensation.

As the very slightest traces of impurity largely affect the diathermancy of air, the strictest precautions were necessary in order to ensure that the sample admitted into the experimental tube was perfectly ...nd dry. For this purpose it was passed through U-tubes filled ...re glass broken into small fragments and moistened with pure ...c acid. It was also found necessary to cover each column of ...be with a layer of dry glass fragments; for the smallest trace

of dust from the corks, or a fragment of sealing-wax not more than the twentieth part of a pin's head in size, was sufficient to vitiate the results if it reached the acid. The drying tubes, besides, required frequent renewal, as the organic matter of the atmosphere, though exceedingly small, after a time introduced disturbance. The carbonic acid was removed by passing the air through another set of U-tubes filled with pure broken Carrara marble moistened with caustic potash.

The front chamber F, and the experimental tube SS′, being both exhausted, the rays of heat from the source C were allowed to fall upon the face of the pile, and the effect of this radiation was compensated by the cube C′, the needle standing at zero. Pure dry air was then allowed to enter the cylinder, but no appreciable motion of the needle could be observed.

The absorption of heat by air is therefore so small that even this delicate test fails to detect it. Oxygen, hydrogen, and nitrogen, when carefully purified, and treated in the same way, showed, like air, no sensible absorption of the radiant heat. Olefiant gas, on the other hand, exhibited a very marked effect. The experimental cylinder being exhausted, and the needle being brought to zero by the compensating cube, olefiant gas was allowed to enter. A marked deflection of the needle, amounting to 70° when the cylinder was filled with gas, was the result, showing that this invisible gas absorbs heat like a solid or liquid. A metal screen was now interposed between the end of the experimental tube and the face of the pile, so that the compensating cube alone might radiate to the pile and produce its full effect. A deflection of 75° was thus obtained, and as, at the commencement of the experiment, the radiations from the two cubes were equal, the deflection 75° represents the total radiation through the exhausted cylinder. Taking as unit the quantity of heat necessary to move the needle from 0° to 1°, the number of units represented by a deflection of 75° was 276, and the number representing a deflection of 70° was 211, so that out of a total of 276 units 211 were absorbed by the gas within the cylinder—that is, the absorption of the gas amounted to about 80 per cent of the whole. The following table exhibits the relative absorption at pressures varying from 1 to 10 inches of mercury :—[1]

[1] The unit employed in this tube is stated by Tyndall to be the amount of heat absorbed by "a whole atmosphere of dried air." This appears to be the quantity of heat corresponding to a deflection of 1° of the thermopile, as some experim[ents] quoted, in which purified air, oxygen, hydrogen, nitrogen, each gave "a d[eflection] of *about* 1° under atmospheric pressure." As the absorption of air seems, [according] to Tyndall, to be largely affected by even a small trace of aqueous vapou[r or other] impurity, the choice of this unit appears ill advised. Any one repeating

OLEFIANT GAS

Pressure in Inches.	Absorption	Pressure in Inches	Absorption
1	90	6	177
2	123	7	182
3	142	8	186
4	157	9	190
5	168	10	193

It thus appears that the absorption increases with the pressure, but not in simple proportion to it or according to any simple law. For very small pressures, however, the absorption was found, as we should expect, to be very approximately proportional to the pressure.

Similar experiments with other gases and vapours were conducted with like success. The results of these are collected in the following table, which shows the exceedingly high absorbing power of ammonia. In order to examine the corrosive gases, the brass experimental tube was replaced by one of glass. The hot water cube was also dispensed with as a source of heat, and replaced by a plate of copper, against which a thin steady gas-flame from a Bunsen's burner was caused to play.

Substance.	Absorption at 1 Atm.	Substance.	Absorption at 1 Atm.
Air	1	Carbonic acid	90
Oxygen	1	Nitrous oxide	355
Nitrogen	1	Sulphide of hydrogen	390
Hydrogen	1	Marsh gas	403
Chlorine	39	Sulphurous acid	710
Hydrochloric acid	62	Olefiant gas	970
Carbonic oxide	90	Ammonia	1195

The examination of vapours was conducted by placing some of the liquid in a test-tube K fitted with a screw-tap carefully cemented on (Fig. 125). By this means it could be attached to a stopcock, and thus connected with the experimental tube. The liquid being introduced, the tube K was connected with an air pump, and the air was completely removed, so that nothing but the liquid and its vapour Vapours.

ments would certainly object to having the most doubtful and last marked of all [...]bstances set up as the standard of reference. Tyndall himself states that [...]tion of these substances is exceedingly small—probably even smaller than [...]it, and he remarks that the more perfectly these gases are purified, the [...] does their action approach that of a vacuum.—*Heat a Mode of Motion,*

remained. The stopcock was then shut, and K was attached to the experimental tube. The latter being completely exhausted, and the needle of the galvanometer standing at zero, the tap attached to K was opened. The vapour was thus allowed to enter the experimental tube silently, and without the slightest commotion, while the manometer attached to the apparatus was carefully observed. In this manner the absorptions of the vapours, mentioned in the following table, were examined at pressures of 0·1, 0·5, and 1 inch respectively :—

Substance	Pressures.		
	0 1.	0 5.	1 0.
Bisulphide of carbon	15	47	62
Iodide of methyl	35	147	242
Benzole . .	66	182	267
Chloroform	85	182	236
Methylic alcohol .	109	390	590
Amylene . . .	182	535	823
Sulphuric ether . .	300	710	870
Alcohol . . .	325	622	
Formic ether . . .	480	870	1075
Acetic ether . . .	590	980	1195
Propionate of ethyl .	596	970	
Boracic acid .	620		

The influence of the temperature of the source on the transmission of radiant heat by vapours is shown very decidedly by the following table. By raising the radiating spiral from a barely visible heat to an intense white heat, the absorption of bisulphide of carbon and chloroform is reduced to less than one-half, and corresponding reductions take place with the other vapours. In some cases even a reversal of the order of their absorbing powers is exhibited.

Vapour.	Source of Heat, a Platinum Spiral.			
	Barely Visible.	Bright Red.	White Hot.	Near Fusion.
Bisulphide of carbon .	6·5	4·7	2·9	2·5
Chloroform . .	9·1	6·3	5·6	3·9
Iodide of methyl .	12·5	9·6	7·8	
Iodide of ethyl . .	21·0	17·7	12·8	
Benzole . . .	26·3	20·6	16·5	
Amylene . . .	35·8	27·5	22·7	
Sulphuric ether .	43·4	31·4	25 9	
Formic ether . . .	45·2	31·9	25 1	
Acetic ether	49·6	34·6	27·2	

Compared with this the absorption order, when the source of heat is a Leslie's cube coated with lamp-black, shows another case of reversal, the iodide of methyl coming above chloroform in the list.

Tyndall also examined the action of perfumes, such as geranium, thyme, and rosemary. Small squares of bibulous paper were rolled up so as to form little cylinders, each about 2 inches in length. One of these paper cylinders was then moistened by dipping one end of it into an aromatic oil, so that the oil crept by capillary action through the paper until the whole became moist. The roll was then introduced into a glass tube which it just filled without being squeezed, and this tube was placed between the drying apparatus and the experimental tube, so that by turning a cock dry air could be gently drawn through the folds of the saturated paper. This air, laden with perfume, passed into the experimental tube, and the absorption due to the perfume could be examined. Taking, as before, the absorption of an atmosphere of dry air to be unity, the absorptions of various perfumes were found as shown in the following table:—

PERFUMES

Substance.	Absorption.	Substance	Absorption.
Patchouli	30	Portugal	67
Sandal-wood	32	Thyme	68
Geranium	33	Rosemary	74
Oil of cloves	34	Oil of laurel	80
Otto of roses	37	Camomile flowers	87
Bergamot	44	Cassia	109
Neroli	47	Spikenard	355
Lavender	60	Aniseed	372
Lemon	65		

Experiments on ozone showed so marked an absorption of radiant heat by this substance that it takes rank with olefiant gas and boracic ether as an absorber.

The diathermancies of several volatile liquids were also examined by Tyndall, in order to determine if the state of aggregation is of paramount importance, or if the absorption depends chiefly on the nature of the individual molecules, and if their deportment towards ...nt heat remains characteristic of the molecule throughout all ...f aggregation. Melloni, in his experiments on the diather... liquids, employed a lamp-flame covered with a glass chimney ... of heat, and the liquid was also enclosed in a glass cell, so

that the radiation was sifted by glass before it entered the liquid. Tyndall, however, desired to have the primitive emission interfered with as little as possible, and to determine the diathermancy of the liquids and their vapours as far as possible under the same conditions. For this purpose he employed, as source of heat, a platinum spiral raised to incandescence by an electric current, and he enclosed the liquid in a rock-salt cell, so that the radiation passed through the liquid, sifted only by rock-salt, as in the case of the vapours and gases. The platinum spiral was enclosed in a glass globe to prevent the disturbing influence of air currents, which render a red-hot spiral an unsteady source of heat in open air. The front of the enclosing globe was provided with an aperture which could be left open, so that the radiation fell directly on the liquid cell, or it could be closed air-tight by a plate of rock-salt, so that the globe could be exhausted, and the spiral allowed to radiate in vacuo. The radiation, in the first instance, was allowed to pass through the empty rock-salt cell, and the galvanometer needle was brought to zero by the compensating cube. The liquid was then poured into the cell, and the deflection of the needle noted. From this deflection the quantity of heat absorbed by the liquid was immediately calculated,[1] and expressed as a percentage of the entire radiation. The results of the investigation are contained in the following table for various thicknesses of the liquid :—

Effect of state of aggregation

Liquid.	Thickness of Liquid in Parts of an Inch				
	0·02.	0·04.	0·07	0·14.	0·27.
Bisulphide of carbon .	5·5	8·4	12·5	15·2	17·3
Chloroform .	16·6	25·0	35·0	40 0	44·8
Iodide of methyl	36·1	46·5	53·2	65·2	68·6
Iodide of ethyl .	38·2	50·7	59 0	69 0	71·5
Benzole	43·4	55·7	62·5	71·5	73·6
Amylene .	58·3	65·2	73·6	77·7	82·3
Sulphuric ether	63·3	73·5	76·1	78·6	85·2
Acetic ether . .	..	74 0	78·0	82·0	86·1
Formic ether .	65 2	76·3	79·0	84·0	87 0
Alcohol . .	67·3	78·6	83·6	85·3	89·1
Water	80·7	86·1	88 8	91·0	91·0

With the same source of heat—namely, a red-hot platinum spiral—the absorption of the vapours of these liquids at a pressure of half an inch of mercury was found to be as follows :—

[1] The altered value of the reflection at the inner surfaces of the cell p[illegible] empty and filled with liquid is neglected, and this quantity may be ve[illegible] able.

Vapour.	Absorption.	Vapour.	Absorption.
Bisulphide of carbon	4·7	Amylene	27·5
Chloroform	6·5	Alcohol	28·1
Iodide of methyl	9·6	Formic ether	31·4
Iodide of ethyl	17·7	Sulphuric ether	31·9
Benzole	20·6	Acetic ether	34·6

Comparing this table with the preceding one, we see that the order of absorption is the same in both as far as amylene. Alcohol and the ethers are still characterised by strong absorption in both lists, although their order becomes inverted in passing from the liquid to the gaseous condition. This inversion, however, arises from the fact that the comparison has been made between liquids taken at a common thickness and vapours at a common pressure and volume. Now, if the equal layers of the liquids employed were converted into vapour, the volumes obtained at a common pressure would not be the same. Hence, in the foregoing comparison, the quantities of matter traversed by the beam of radiant heat are not in the same proportion in the two cases, and to render the comparison strict they ought to be proportional. The correction in this respect is easily applied when we know the specific gravities of the liquids and their vapour densities, and when applied it is found that the order in both lists as regards absorption becomes exactly the same, so that the discrepancies appearing in the foregoing tables are removed; or, in other words, it is proved that for heat from the same source the order of absorption for liquids and their vapours is the same.

It appears then that in the main the molecules maintain their characteristics as absorbers of radiant heat, although the state of aggregation changes, and if any inference be allowed we should expect that aqueous vapour would be exceedingly opaque to thermal radiation, for, as we have already seen, pure water stands at the bottom of the list as a transmitter of radiant heat.

This anticipation as to the opacity of aqueous vapour seems to have been fully verified by the experiments of Tyndall, but subsequent investigations by Magnus and others by different methods brought the matter into warm dispute, for, while Tyndall with one form of apparatus found the absorption of aqueous vapour to be enormously greater than of dry air, Magnus with another found no such difference of ng power, while more recently Lecher and Pernter[1] found that ption of aqueous vapour like that of air was quite insensible.

k. *Akad. der Wissensch. in Wien*, July 1880; *Phil. Mag.*, Jan. 1881.

In face of these very different results on the absorption of such an important vapour as that of water, by men who had already proved themselves possessed of the highest experimental skill, it may be well to give here a brief account of the methods adopted and of the objections raised by each to the apparatus of the other.

Aqueous Vapour

243. Tyndall's Experiments.—The low diathermancy of pure water prepared Tyndall to expect that aqueous vapour would also prove itself highly opaque to radiant heat, and this expectation was surprisingly confirmed. Pure dry air being admitted into the experimental cylinder a deflection of scarcely 1° was observed. Making a similar experiment with the undried air of the room the needle moved through 48°. This corresponded to an absorption of 72—that is to say, the aqueous vapour contained in the air absorbs 72 times the quantity of heat absorbed by the air itself. This figure is rendered all the more surprising when we remember that the quantity of vapour in the air amounts to less than one-half per cent.

This result, if true, is of such importance in the science of meteorology that it ought to be subjected to the most careful examination, and the closest scrutiny of the whole matter seems to have been carried out by Tyndall. Rock-salt is a hygroscopic substance, and it might be supposed that the aqueous vapour condenses on the faces of the rock-salt plates which close the ends of the experimental tube, and that in this manner a thin film of aqueous salt solution is formed, which, as appears from Melloni's tables, is highly opaque to radiant heat, though not more opaque than pure water. The question, therefore, arises whether in the foregoing experiment the absorption observed is not in reality due to thin films of moisture deposited on the plates. The aqueous vapour might also become condensed on the walls of the cylinder so that the reflection from its sides might become seriously diminished, and the apparent absorption might arise from this diminution of the reflecting power of the interior surface of the cylinder. So, again, it has been suggested by Magnus that the London air is always impure and to some extent misty from suspended matter, which, though it be so small as to escape the eye, yet may be sufficient to stop by reflection a conside[illegible] portion of the radiant heat. In order to meet this objection[1] T[illegible]

[1] If such an objection were allowed, *invisible* particles or globules mi[illegible] be introduced to explain all absorption by gases.

examined samples of air brought from the Isle of Wight and other localities, but always obtained the same result. The other objections are more serious, and demand special precautions and modifications of the apparatus. The effect of a variation of reflecting power of the inner surface of the tube might be determined, at least to some extent, by blackening the inside, but this method of experiment does not appear to have been prosecuted by Tyndall with sufficient fulness. Some experiments are described in which the inside of the cylinder was lined with black for *half* its length, and from these it was concluded that the high absorption obtained for aqueous vapour did not arise from this cause. Fuller experiments, in which the whole of the interior of the tube was blackened, would have been more satisfactory, and it is difficult to understand why half-measures were resorted to in this important matter.

With regard to the first objection—namely, the deposition of moisture on the rock-salt plates—the precautions taken were as follows. In the first place, it was assumed that the plate nearest the source of heat always remained free from this source of error on account of its proximity to the source of heat. The distant plate was assumed to be the only one in danger, and to protect it one of the conical reflectors was removed from the pile and placed within the cylinder, with its narrow end abutting against the rock-salt plate, while the space between it and the metal tube was filled with fragments of fused chloride of calcium. The face of the pile from which the reflector was removed was then brought close up to the rock-salt plate, and the experiments were proceeded with as before. The chloride of calcium kept the circumferential portions of the plate perfectly dry, and the whole beam of radiant heat was converged by the reflector on the central part. With this arrangement it was supposed that the deposition of moisture on the plate was impossible. On examining the plate, even with a lens, no trace of moisture could be detected on it, the polish remaining perfect throughout.

Further, the plates of rock-salt were dispensed with entirely, and the experimental tube was left open at both ends, the arrangement of the apparatus being as shown in Fig. 126. In order to avoid agitation of the surrounding atmosphere while the air was being introduced into the open tube, it was arranged that dry air could be allowed to enter the tube slowly through the tap C, while D was connected with an air pump which was slowly worked, so that the dry air was drawn from C towards D. Thus throughout the central portion of the tube a column of moist air could be displaced by dry air, and *vice versâ*.

In making an experiment with this apparatus the tube was at first

filled with the common air of the laboratory, and the needle was brought to zero by the compensating cube. Dry air was then allowed to enter slowly and displace the moist air which initially occupied the tube. As soon as the dry air was allowed to enter the needle commenced to move and finally stood at a deflection of 45°. When the supply of dry air was cut off the deflection commenced to fall, but with great slowness, indicating a slow diffusion of the aqueous vapour through the dry air of the tube. If the pump was worked the dry air was removed more quickly and the needle sank rapidly to zero. The result of all these experiments was, therefore, to confirm the conclusion already arrived at by Tyndall as to the high absorptive power of aqueous vapour for radiant heat.

Humid air was also tested at various pressures, and the results verified the anticipation that the absorption varies directly as the

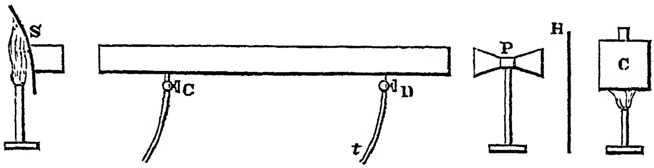


Fig. 126.

quantity of vapour present. The third column of the following table was calculated on this supposition, and it can scarcely be supposed that results so regular as these can be due to condensation of the vapour on the interior surface. Besides, under the pressure of 5 inches the quantity of vapour within the tube is less than one-sixth of the quantity necessary to saturate the space—a dryness unapproached by our driest days.

HUMID AIR

Pressure	Absorption. Observed.	Absorption. Calculated.
5 inches	16	16
10 „	32	32
15 „	49	48
20 „	64	64
25 „	82	80
30 „	96	96

In conclusion, it may be remarked that as the air generally operated with was that of the laboratory, there appears to be no

particular reason why the moisture should condense on the inside surfaces of the plates more than on the outside, and it is well known that a plate of rock-salt exposed in the open air is highly diathermanous, which shows that opacity to radiant heat is not introduced in this manner in the open air.

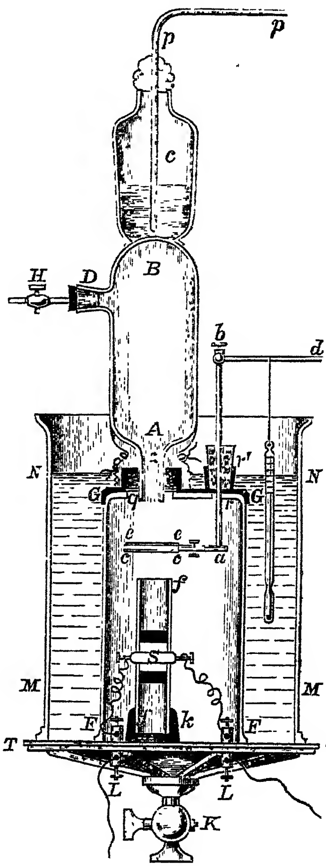


Fig. 127.

244. Magnus's Experiments.—The experiments of Professor Magnus[1] on the diathermancy of gases were conducted chiefly with the apparatus shown in Fig. 127. This consisted of two glass vessels having their bottoms fused together, one being much larger than the other. The smaller one, C, stood upright, and acted as the source of heat, being partly filled with water which was kept at the boiling point by a current of steam passed through the tube *pp*. The larger vessel BF was turned mouth downwards, and had its mouth FF ground down so that it could be placed like an ordinary receiver on the plate of an air pump and exhausted, while, by means of the cocks H and K, it could be filled with any gas desired. It was surrounded by a water bath, MM, kept at 15° C. Within this experimental space a thermopile S, with its axis vertical, was attached to the plate of the air pump, and one face was directed towards the common surface of the two vessels which had been fused together. This surface was heated to 100° C. by the hot water and acted as the radiator. The pile could be exposed to the radiation or protected from it at pleasure by means of a movable screen, *ce*, and the entire space between the pile and the radiating surface could be rendered a vacuum or filled with a gas.

Experimenting in this way, Magnus found that air and oxygen intercepted over 11 per cent of the heat radiated by the source, while hydrogen cut off more than 14 per cent. Tyndall, on the other hand,

[1] Magnus, *Pogg. Ann.*, vol. cxii. p. 531; *Phil. Mag.*, vol. xxii., 1861.

after using every precaution, found that these gases were practically vacua to radiant heat. With the more powerful compound gases, on the other hand, Tyndall found a considerably stronger action than Magnus. Thus with olefiant gas Magnus found an absorption of less than 54 per cent, whereas Tyndall obtained more than 72. This result, however, was to be expected, as the length of gas traversed by the radiant heat in the experiments of the former was under 15 inches, whereas in those of the latter it was 33. The following table is taken from Magnus's memoir :—

Substance	Transmission	Substance.	Transmission.
Vacuum	100	Protoxide of nitrogen .	74·06
Air	88·88	Marsh gas . .	72·21
Oxygen	88·88	Cyanogen .	72·21
Hydrogen .	85·79	Olefiant gas	46·29
Carbonic acid	80·23	Ammonia .	38·88
Carbonic oxide .	79·01		

Magnus also describes a series of experiments in which the source of heat was a powerful gas-flame, surrounded by a glass chimney, and provided with a parabolic mirror to reflect and concentrate the rays. In this series the foregoing apparatus was dispensed with, and the gas under examination was enclosed in a glass tube 1 metre long and 35 mm. in diameter, the two ends of which were stopped, not by plates of rock-salt, as in Tyndall's experiments, but by plates of glass 4 mm. thick

Two series of experiments were executed with this tube, one in which the interior surface was covered with black paper, and the other in which it was uncovered. The former method had been previously employed by Dr. Franz, and the results obtained by Magnus in the case of air and oxygen agree closely with those of Franz, the former obtaining an absorption of about $2\frac{1}{2}$ per cent for these gases in the blackened tube, while Franz obtained about 3 per cent.

In the case of the unblackened tube, however, the absorption was found to be much more considerable. Here air and oxygen cut off 14·75 per cent, while hydrogen intercepted 16·23 per cent. This great difference between the actions in the unblackened and the blackened tubes is ascribed by Magnus to a change of quality of the heat produced by its reflection at the interior surface of the glass. The results are contained in the following table :—

	Blackened Tube.	Unblackened Tube.
Vacuum	100	100
Air	97·56	85·25
Oxygen	97·56	85·25
Hydrogen	96·43	83·77
Carbonic acid	91·81	78·08
Carbonic oxide	91·85	72·05
Protoxide of nitrogen	87·85	75·50
Marsh gas	95·87	76·61
Olefiant gas	64·10	59·96
,, ,,	65·39	60·99
Ammonia	58 12	55·00

We now come to the case of aqueous vapour. With both the gas-flame and the boiling water as sources of heat, Magnus found the effect of dry air to be precisely the same as that of moist air saturated with vapour. He concluded from his experiments "that the water present in the atmosphere at 16° C. exercises no perceptible influence on the radiation." The vast difference obtained by Tyndall in the behaviour of moist and dry air to radiant heat has been already noticed, and as these discrepancies were attributed by Magnus to condensation on the interior surface of Tyndall's experimental tube and on the rock-salt plates, so Tyndall in turn attributed them to sources of error inherent in Magnus's method of experiment. Thus Magnus in his first apparatus (Fig. 127) avoided the use of plates of any kind; but in order to do this he was compelled to bring his gas into direct contact with his source of heat. Convection currents may in this manner be set up within the experimental chamber, and Tyndall held that the results obtained by Magnus were largely affected by this source of error, the greater convection of hydrogen also accounting for the difference obtained by Magnus between this gas and air. So also Magnus used glass plates to close his experimental tube, and these, according to Tyndall, become heated and radiate to the pile as secondary sources. On the introduction of a gas, however, the plates become cooled by convection and conduction, and the effect of this cooling on the pile is the same as if a true absorption took place within the gas. Aqueous vapour.

245. Experiments of Lecher and Pernter.—More recently a series of experiments on the absorption of radiant heat by gases and vapours has been published by Ernst Lecher and Joseph Pernter;[1] but these new investigations, instead of settling the question in dispute between Tyndall and Magnus as to the comparative absorptions of dry

[1] Lecher and Pernter, *Sitzb. der k. Akad. der Wissensch. in Wien*, July 1880; *Phil. Mag.*, January 1881.

and moist air, place the whole matter in a state of greater uncertainty. For whereas Tyndall found an exceedingly low absorption for dry, and a high absorption for moist air, while Magnus found the same absorption for both, and that tolerably high, the results of the experiments of Lecher and Pernter show practically no absorption for either; or, in other words, both dry and moist air act as a vacuum towards radiant heat.

The method adopted in these investigations was similar to that employed by Magnus, the source of heat and the thermopile being in the same chamber as the gas under examination. In order to avoid convection currents, however, a special heating arrangement was adopted, whereby the radiating surface was suddenly brought to 100° C. by directing a jet of steam against it. The apparatus was for this reason a considerably modified form of that of Magnus. The thermopile and gas under consideration were contained in an inverted glass bell-jar, with the open end upwards. The pile was placed on a wooden support on the bottom of this vessel without a conical reflector or any similar arrangement for collecting the rays, and its upper face, which was carefully covered with lamp-black, was directed upwards towards the source of heat, while the lower face was protected against changes of temperature by a packing of cotton-wool. The mouth of the bell-jar, or experimental chamber, was closed by a special vessel which carried the radiating surface, and replaced the upper or hot water vessel in the apparatus of Magnus. The radiating surface was a thin copper plate covered with lamp-black, and was situated at a distance of 310 mm. from the pile.

In making an experiment the temperature of the whole apparatus was allowed to become uniform, and then a jet of steam was suddenly directed against the radiating plate. By keeping the boiler constantly filled to the same level, and heating it with a steady flame, it was arranged to always direct equal quantities of vapour on the plate in each of a series of experiments, so that the plate was always heated to the same extent. The steam tube was put into place by one person, while the galvanometer was observed by another, and the whole time of an observation occupied about one minute and a half. In this way it was supposed that all error arising from convection currents was completely avoided, for it was not until the sixth or eighth reversal of the needle in each experiment that the effects of currents became perceptible.

In this manner it was found, as has been already mentioned, in opposition to the results of Tyndall, that the absorption of aqueous vapour is excessively small, and, as in the case of air, practically im-

perceptible. They thus confirm the view of Magnus with regard to aqueous vapour, but they contradict his result for air. The numbers obtained for other gases agree fairly well with those given by Tyndall, but in the case of vapours considerable differences exist.

246. Comparison of Results.—These contradictory results, obtained by most careful and experienced experimenters, arise undoubtedly from the great difficulties attending observations in this department. No method seems to have been yet employed which is perfectly free from objection. These differences are strikingly illustrated in the case of air. Thus Tyndall obtained no appreciable absorption for a layer of air 1·22 metre thick, and this result is supported by the work of Lecher and Pernter. Magnus, on the other hand, found that a layer of air 275 mm. thick absorbed 11 per cent of the radiation, and Buff[1] believed that he observed an absorption of 40 per cent by a layer of air only 45 mm. thick!

The method of experiment in which the thermopile and source of heat were both in the experimental chamber containing the gas has been employed by Magnus, and then by Garibaldi[2] and Buff. Tyndall justly objects to this method on account of the convection currents, and this source of error appears to have been recognised by Magnus, as he did not return to the question. Buff endeavoured to avoid it by rapidly heating the radiating surface, and the same plan, we have seen, was adopted by Lecher and Pernter. Garibaldi employed a concave mirror to concentrate the heat rays, and obtained the enormous absorption of 92 per cent for aqueous vapour!

Tyndall, on the other hand, chiefly employed the method in which both the source of heat and the thermopile are outside the experimental space. This necessitates the use of diathermanous plates to close the ends of the experimental tube. For this purpose glass plates were employed by Franz and Magnus, and the objections to glass for this purpose have been considered. Tyndall employed rock-salt, which is much more highly diathermanous, but according to Tyndall's own experiments this substance is not perfectly diathermanous, and it is just possible that it may absorb the same rays as those intercepted by air. This objection has been raised by Buff, and, if true, the radiation would be sifted before entering the air in the tube, and the low absorption obtained by Tyndall for air would be accounted for. This objection does not appear, however, to have been confirmed, and Tyndall[3] seems to have completely refuted

[1] Buff, *Pogg. Ann.*, vol. clviii. p. 177, 1876; *Phil. Mag.* (5), vol. iv. p. 401, 1877.

[2] *Il Nuovo Cimento*, 2nd Series, vol. iii., 1871.

[3] Tyndall, *Proc. Roy. Soc.*, vol. xxx. p. 19, 1879.

it. The employment of rock-salt seems, therefore, to be permissible in experiments with dry gases, since the percentage of rays absorbed does not appear to be materially influenced by its imperfect diathermancy. The case is different, however, with vapours, for these may condense on the plates and on the walls of the experimental tube, and thus form an important source of error.

SECTION IV

RADIOMETERS

247. The Differential Thermometer.—In the preceding investigations on the laws of cooling, the temperatures were registered by ordinary liquid-in-glass thermometers. The general study of radiation, however, required some much more sensitive temperature-registering apparatus, and the great advances in this subject followed the invention of more and more delicate instruments for the detection of feeble radiation. All the most valuable of these instruments depend in principle on the thermoelectric properties of matter.

The first instrument specially invented for the study of radiant heat was a species of air thermometer designed by Sir J. Leslie, and

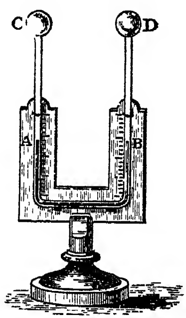


Fig. 128.

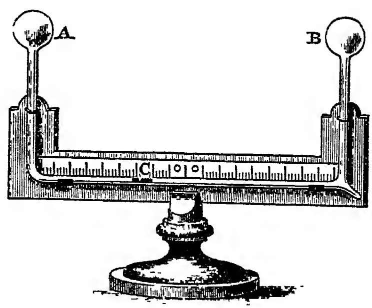


Fig. 129.

in his hands this instrument (which is now of little more than historic interest) rendered important service. In Leslie's form of the apparatus (Fig. 128) two equal bulbs, C and D, filled with air are connected, as shown in the diagram, by a narrow bent tube which contains some non-volatile liquid, such as sulphuric acid. When the two bulbs are at the same temperature, the liquid stands at the same level in the two arms of the tube; but if one of the bulbs is heated, the pressure of the air within it increases, and the liquid is forced towards the

cooler bulb by the expanding air in the warmer. The level of the liquid in the arm to which the warmer bulb is attached will thus be lower than the level in the other arm, and from the difference of level the difference of temperature may be estimated.

Thus since the bulbs are equal, and the liquid stands at the same level in the arms when the temperature is the same, it follows that the mass of air in one bulb is the same as that in the other. If the zero mark of the scale be the point at which the level of the liquid stands when the two bulbs have the same temperature, and if v denotes the volume of each scale division of the tube, then when the surface of the liquid stands n divisions below the zero mark in one arm, and n divisions above it in the other, the volumes occupied by the air in these arms will be V and $V+2nv$ respectively, and the corresponding temperatures of the bulbs will be Θ and $\Theta+\Delta\theta$. In addition, the pressure in the colder bulb will be P, and if the pressure due to the weight of each scale division of the liquid be p, the pressure in the warmer bulb will be $P+2np$, and consequently applying the equation $PV=R\Theta$ to each arm we have

$$\frac{PV}{\Theta}=\frac{(P+2np)(V+2nv)}{\Theta+\Delta\theta}=\frac{2nPV}{\Delta\theta}\left(\frac{p}{P}+\frac{v}{V}\right),$$

since p/P and v/V are both small, the final member being obtained by subtracting the numerator and denominator of the first from the corresponding terms of the second. The equality of the first and third members gives at once

$$\Delta\theta=2n\Theta\left(\frac{p}{P}+\frac{v}{V}\right).$$

If the colder bulb be at zero centigrade, then $\Theta=\frac{1}{a}$, and further, if the volume V be replaced by V_0, the volume of either bulb up to the zero mark, and P by P_0, the pressure when the liquid stands at the same level in the two arms, we have the approximate equation

$$\Delta\theta=\frac{2n}{a}\left(\frac{p}{P_0}+\frac{v}{V_0}\right).$$

A modified form of Leslie's apparatus was designed by Count Rumford, which possesses much greater delicacy than the original. In Rumford's form (Fig. 129) the liquid column is reduced to a simple index moving along the horizontal part of the tube which joins the bulbs, so that the pressure in one bulb is always equal to that in the other.

If the index be displaced n divisions from the zero mark, we have in this case

$$\frac{V}{\Theta}=\frac{V+2nv}{\Theta+\Delta\theta}=\frac{2nv}{\Delta\theta},$$

where V is the volume, and Θ the temperature of air in the colder arm.

Hence

$$\Delta\theta=2n\Theta\frac{v}{V},$$

or approximately

$$\Delta\theta=\frac{2n}{a}\frac{v}{V_0}.$$

A modified form of the differential thermometer has also been devised by Matthiessen, which can be used conveniently with liquids. For this object the arms to which the bulbs are attached are bent round twice at right angles, so that the bulbs hang downwards, and can be easily dipped into liquids, and the difference of temperature of two liquids can thus be registered. The differential thermometer, when employed as a radiometer, is less sensitive than a simple air thermometer, for when the index moves under the expansion of the air in one of the bulbs an increase of pressure is set up in the other, and this reduces the displacement of the index which would otherwise occur.

248. The Thermopile.—The thermopile is probably the most celebrated instrument ever designed for the study of radiant heat, for although it has been surpassed in delicacy and quickness of action by more recent forms of apparatus, yet it is to the services of the thermopile that we owe the researches of Melloni and Tyndall, as well as nearly all the advances that have since been made in the study of radiation. This instrument was invented by Nobili, and in its action is based on a discovery made by Seebeck about 1820, that when two wires of different metals are joined end to end so as to form a closed circuit, then when one of the junctions is heated, or cooled, an electric current passes round the circuit, and this current continues to flow as long as any difference of temperature exists between the two junctions.

The most elementary form of such an apparatus is shown in Fig. 130, where A and B are the junctions of two dissimilar wires, the wires being soldered together at these points, and one of them being in circuit with a galvanometer G. As long as A and B are at different temperatures, a current passes round the circuit and deflects the needle of the galvanometer. When the two junctions are at the same temperature, as when they are both immersed in the same bath, there is no current, and the galvanometer needle remains steady, but as the difference of temperature increases the current strength increases, and the deflection of the needle augments accordingly.

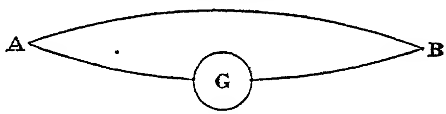


Fig 130.

We have here, therefore, a means of estimating differences of temperature, and on this property a scale of temperature might be founded by saying arbitrarily that the current strength in the circuit is proportional to the difference of the temperatures of the

two junctions just as legitimately as on the expansion of mercury or any other liquid. We have, however, already chosen the air, or perfect gas thermometer as our standard of reference, and, understanding temperature to be measured in this way, it is found that the current strength in a thermoelectric circuit is not exactly proportional to the difference of the temperatures of the two junctions, but for small differences it is nearly so. The electromotive force gradually increases with the difference of temperature; but, as Cumming discovered, if one junction is kept at a constant temperature, while the temperature of the other is gradually raised, the current strength does not go on continually increasing, but ultimately reaches a maximum, after which it decreases and ultimately falls to zero again, and becomes reversed, so that the deflection of the galvanometer vanishes, not only when the two junctions have the same temperature, but also again when they are at very different temperatures. The mean of the temperatures of the two junctions when the latter occurs is found to be always the same for the same pair of metals, and is called their neutral[1] temperature. The existence of this phenomenon utterly disqualifies the thermoelectric couple as a standard of measurement of temperature, and for all purposes of measurement the instrument must be empirically graduated by a direct comparison of its indications with those of some standard instrument.

The thermopile, as usually constructed, consists not of a single pair of wires, but of several pairs arranged in such a way that a given difference of temperature produces a much more marked deflection of the galvanometer than that which would be caused by a single pair. This arrangement is indicated in Fig. 131, which shows a system of pairs of little bars of two different metals soldered together, and arranged so that the alternate bars are of the same metal, and thus at each junction two dissimilar metals are soldered together. If the system is in circuit with a galvanometer G, and if all the lower junctions are at one temperature, while all the upper junctions are at another, then the electromotive force of the system will be equal to that of a single pair multiplied by the number of pairs.

[1] Since the electromotive force vanishes when the temperatures θ_1 and θ_2 of the two junctions are equal, it follows that $\theta_1 - \theta_2$ must be a factor of the expression for the electromotive force. In the same way, if the neutral temperature be θ_0, then the electromotive force vanishes when $\frac{1}{2}(\theta_1+\theta_2)=\theta_0$, and, therefore, $\theta_0 - \frac{1}{2}(\theta_1+\theta_2)$ must also be a factor. The expression for the electromotive force must therefore be of the form

$$A(\theta_1-\theta_2)\{\theta_0-\tfrac{1}{2}(\theta_1+\theta_2)\}.$$

In practice about twenty-five pairs, each consisting of a small bar of antimony soldered to a similar bar of bismuth, are arranged, as shown in Fig. 132, in the form of a rectangular parallelopiped, the pieces being carefully insulated from each other by some insulating material, such as thin paraffined paper.

In conjunction with a thermopile it is necessary to use a galvanometer, and in constructing a delicate instrument it is necessary to pay due attention to the proper construction of the latter. With a given pile the best galvanometer to work with is one whose resistance is equal to that of the pile, and in constructing a galvanometer of some predetermined resistance, what is required is to wind it with as many turns of wire as possible, especially near the inside, where each turn produces the greatest effect. The question also arises as to what number of couples will be most advantageous in a thermopile. Now it is clear that the face of the pile need not

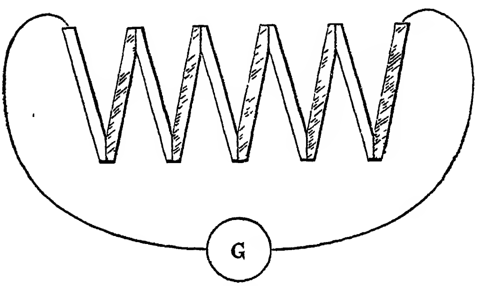
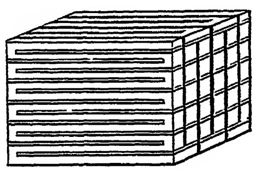


Fig. 131.



Thermo-pile.

Fig. 132.

exceed the area on which the radiation can be concentrated, and if the number of bars in a given area be doubled the electromotive force will be doubled, but the resistance of the pile will be increased four times, for not only are there twice the number of bars, but the cross-section of each is halved, so that if the resistance of the galvanometer be made four times as great by winding twice the number of turns of wire in the same space, the resistance of the whole circuit will be four times as great, and, consequently, the current will be half as great, but as it circulates round the needle twice as often, the deflection will be the same as before. Hence the deflection will be the same with one pair and a corresponding galvanometer as with many pairs filling the same space. This is true only so long as the resistances of the connecting wires can be neglected, and as it is often necessary to work with the pile at some distance from the galvanometer, the number of pairs in the pile should be considerable, for, as they are increased, the effect of the connecting wires becomes less and less.

Another point of practical importance in favour of a large number of pairs is, that in this case the electromotive force is large, and the disturbing effects of accidental electromotive forces are of smaller consequence—such, for example, as the thermoelectric effects which may occur at binding screws subject to accidental changes of temperature by handling, etc., or by connecting wires moving in the earth's magnetic field.

The difficulties attending the use of the thermopile as a sensitive and accurate radiometer arise from the comparative slowness of its indications and the length of time required for it to return to zero. These defects unfit it for many delicate experiments.

249. The Bolometer.—An instrument depending on the change of electric resistance with temperature, and surpassing the thermopile in delicacy and merit as a radiometer, was brought out in 1881 by Professor Langley,[1] and named the bolometer or actinic balance. This instrument was designed for the study of the distribution of heat in the solar spectrum, and in the hands of the inventor it has proved itself a fruitful means of investigation in this department, not merely detecting the presence of very feeble radiation, but also, as its name indicates, furnishing a measure of its amount (Fig. 133).

The working part of the instrument consists of a thin strip of steel, platinum, or palladium foil, resembling a grating or system of parallel elements of the same metal joined so as to form a continuous circuit. This system of strips, or grating as we shall call it, is punched from a thin sheet of the foil, giving strips about 1 cm. long, $\frac{1}{2}$ mm. wide, and $\frac{1}{100}$ to $\frac{1}{500}$ mm. thick, this process being preferable to that of soldering the ends of the strips together. The grating is exposed to the radiation, and is placed in one of the arms of a Wheatstone's bridge, and a similar grating, screened from all radiation, is placed in another arm of the bridge, and used as a counterbalancing resistance. This arm also includes a resistance which can be varied, so that exact balance may be obtained in the galvanometer circuit. A current from a battery of one or more Daniell's cells divides

[1] Langley, *Proc. American Acad. of Arts and Sciences*, vol. xvi. p. 342, 1881.

The earliest account of an instrument, depending on change of electrical resistance, for measuring or detecting heat, appears to be that of Svanburg (*Pogg. Ann.*, vol. xxiv. p. 416, 1851), who, for this purpose, introduced a flat spiral of blackened copper wire into one of the arms of a Wheatstone's bridge. Dr. Baur has published two papers on the Bolometer (*Proc. Berlin Phys. Soc.*, March 3, 1882; *Ann. der Ph. und Ch.*, vol. xix. p. 12, 1883). He constructed his gratings of tinfoil, blackened with platinic chloride, and this sensitive surface acquires its final temperature almost instantaneously. The two resistances are placed side by side, so that, by the movement of a shutter, the radiation may be allowed to fall on one or the other alternately, and thus double the effect.

itself between the two systems, one-half passing through each. When the two currents are equal, the needle of the galvanometer remains motionless, but when heat falls upon the exposed system, the resistance of that set increases, and the current passing through it is diminished, with a consequent deflection of the galvanometer. By this means a change of temperature of so little as $\frac{1}{10000}$ of a degree centigrade or less may be measured; and from the excessive thinness of the strips, they take up and part with heat almost instantaneously, so that this instrument is much more prompt in its action than the thermopile. It is also much more accurate, for Professor Langley

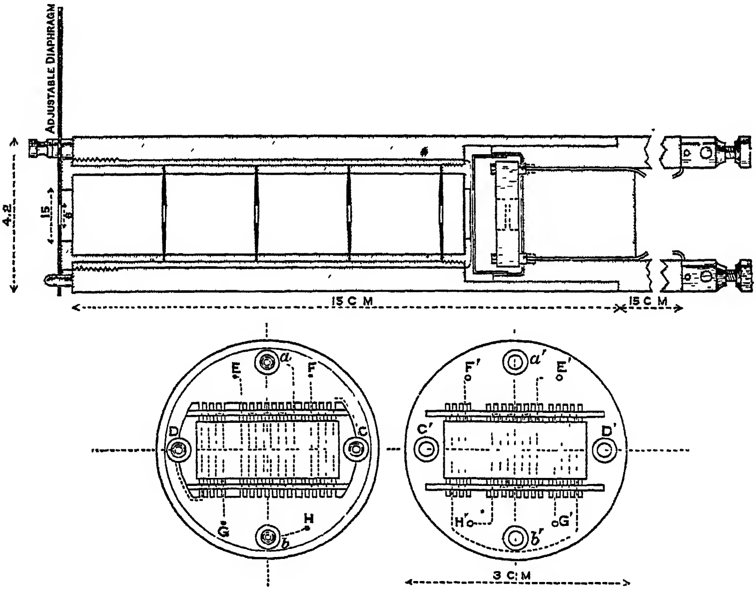


Fig. 133.

estimates the error of a single measure with it at less than 1 per cent.

To protect the grating from air currents and sudden changes of temperature it is enclosed in a chamber lined with copper to secure an equable distribution of temperature. This chamber is contained in a long cylinder of wood or ebonite, which is also furnished with four or more coaxial cardboard diaphragms pierced with apertures 6 mm. in diameter, and separated by ebonite rings, which form a succession of drum-like chambers through which the radiation passes, and which effectually stop air currents from without. The mouth of this cylinder is furnished with a revolving cardboard disc with suitable stops which

admit or shut out the radiation at pleasure. At the back of the copper-lined chamber containing the strips is a layer of solid non-conducting material through which the connecting wires pass to binding screws, and behind this is a chamber containing the adjustable resistance by which the two arms of the bridge may be counterbalanced to perfect equality. It is advisable to have the two arms as equal as possible at first, since, if unequal, the increment of resistance of the larger caused by a general rise of temperature exceeds that of the smaller, necessitating a frequent readjustment of the variable resistance, and producing a "drift" of the galvanometer needle which slowly changes its direction according as the temperature of the room rises or falls. A similar drift due to different causes also affects the thermopile when the galvanometer is very delicate.

The requirements of the instrument necessitate in the construction of the grating the use of a metal of high electrical resistance, and the resistance of which changes considerably with change of temperature. At the same time the metal requires to be tenacious as well as ductile, and not liable to become oxidised or changed by exposure to the air. The metals which seem to best meet these requirements are steel, platinum, and palladium.

The bolometer has been quite recently applied by Tschqlieeff[1] in the measurement of dielectric constants, and in the detection of Hertzian waves.

It seems difficult to believe that an instrument such as the bolometer, which depends in its action on the change of resistance of a wire with temperature, a variation which is always comparatively small, could be made to surpass or even approach in delicacy as a radiometer a properly-designed and carefully-constructed instrument such as the thermopile, which depends on the thermo-electromotive force developed by difference of temperature at the junctions of two dissimilar metals. If an instrument of the latter class could be constructed as delicately as Langley's bolometer, a better result ought to be obtained. The one point, however, in which the bolometer has a great advantage is the smallness of the mass of the part to be heated, whereas in the thermopile, however delicate the bars may be, the mass is so large that the rate of heating and the ultimate rise of temperature must be comparatively small. A thermopile cannot be made with bars of antimony and bismuth as thin as the wires of the bolometer, and such a construction would be necessary in order to use the thermo-electromotive force with the same advantage as the variation of resistance is in the bolometer. If the connecting wires had no

[1] Tschqlieeff, *Journal de la Société Physico-Chemique Russe*, 1890, p. 115.

resistance no advantage would be gained by having more than a single pair of bars in the pile, provided the galvanometer were properly proportioned, and the mass of the instrument would be greatly diminished. The problem on hand is then reduced to the invention of some delicate method of detecting the current in a single couple, and the solution of this problem has been given by Professor C. V. Boys in the beautiful instrument named the radio-micrometer.

250. The Radio-Micrometer.—The active part of the instrument devised by Professor Boys [1] (the radio-micrometer) consists of a very light circuit (Fig. 134) composed of a single loop of fine bare copper wire, to the lower ends of which a pair of very light bars of antimony and bismuth [2] are soldered. These bars form a thermoelectric couple, and the circuit is completed by soldering them side by side at their lower ends to a very small disc of thin copper, or (if the instrument is intended for spectrum analysis) to a very narrow strip of copper foil on which the radiation is received. When radiation falls on this disc the lower junction of the couple becomes heated and a current traverses the circuit, and in order to detect this the circuit is suspended in a strong magnetic field (Fig. 135), in which it is deflected, as in the case of Thomson's siphon recorder, or the moving coil galvanometer.[3] It thus possesses all the advantages of an ideal thermopile of exceedingly small mass, while the current is detected without the aid of a separate galvanometer.

The circuit is suspended by being attached to the lower end of a very thin capillary glass tube, 5 cm. long, which is suspended by a quartz fibre made by the bow-and-arrow process.[4] Close to the top

[1] C. V. Boys, *Phil. Trans.*, vol. clxxx., A, p. 159, 1888-89; *Journ. Soc. Arts*, 11th October 1889.

[2] Alloys of these metals are preferable. Thus, as Professor Boys points out, 32 Bi+1 Sb is better than Bi in the ratio 10 : 9, and 14 Bi+1 Sb is better than Sb, or again 10 Bi+1 Sb and Sb and Cd in equivalent proportions are still better, but the latter alloy is troublesome to work. The dimensions of the circuit employed were: thermoelectric bars $\frac{1}{3} \times \frac{1}{50} \times \frac{1}{200}$ inch; No. 36 copper wire made into a circuit 1 inch long and about $\frac{1}{10}$ inch wide; a copper heat-receiving surface about $\frac{1}{10}$ inch diameter, and blackened on the side exposed to the radiation; mirror $\frac{1}{10}$ inch square and $\frac{1}{200}$ inch thick. The quartz fibre was 4 inches long and $\frac{1}{5000}$ inch thick, and the weight of the complete circuit was half a grain.

[3] This principle of fixed magnet and movable coil appears to have been employed by Sturgeon as early as 1836, and M. D'Arsonval, on 5th February 1886, exhibited, at a meeting of the Physical Society of France, an instrument called by him the thermo-galvanometer, with which the radio-micrometer of Boys was identical in all essential respects. In detail, however, the two instruments differ essentially; but when Professor Boys became acquainted with the work of D'Arsonval, he at once fully admitted the claim of the latter to priority.

[4] See *Phil. Mag.*, June 1887.

of the tube a very light galvanometer mirror is fastened, so that any heat which may fall upon it has no influence on the circuit below. The circuit of copper wire hangs in a narrow hole within a mass of brass situated between the pole-pieces, NS, of a powerful permanent steel magnet and the little bars of antimony and bismuth (or alloy) hang below within a cavity drilled out of a mass of soft iron, where the radiation falls upon the junction through a transverse aperture (Fig. 135). Thus, while the circuit hangs in a strong magnetic field, the central mass of soft iron (shaded dark in Fig. 135) screens the antimony and bismuth, and prevents any trouble arising

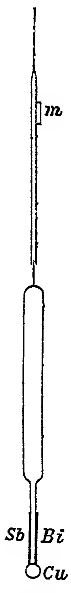


Fig. 134.

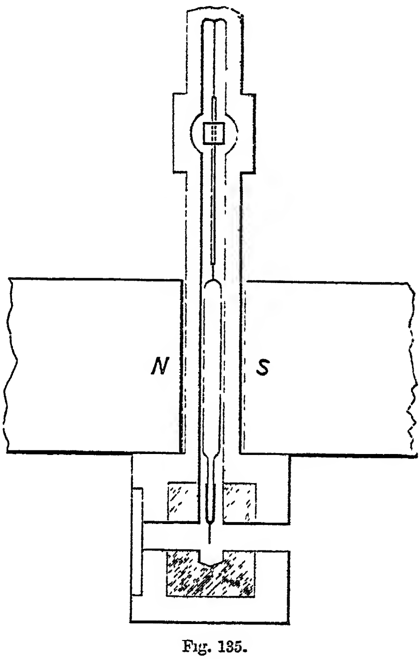


Fig. 135.

from diamagnetism. Such disturbances have been so completely overcome that a strong magnet may be moved about close to the instrument without affecting it.

Figure 136 shows the whole instrument enclosed within a thick wooden cover (dotted outline), which prevents external radiation and draughts from falling upon and unequally warming the metal cavity. Attached to this wooden cover is a paper tube, which projects in front of the chamber containing the thermoelectric pair. The radiation enters through this tube, and it is fitted with a series of diaphragms such as Langley used with his bolometer. A glass window closes the

back of the chamber, so that it is possible to see whether the radiation falls upon the copper disc as intended, while the glass protects the junction from the dark heat of the eye.

Besides its extreme quickness of action and delicacy, the advantages claimed for this instrument are its freedom from extraneous thermal and magnetic influences, the circuit being suspended in a cavity within a mass of metal. It has also a constant and definite zero, given by the control of the suspending fibre, and this being of quartz, the difficulties caused by the uncertain behaviour of

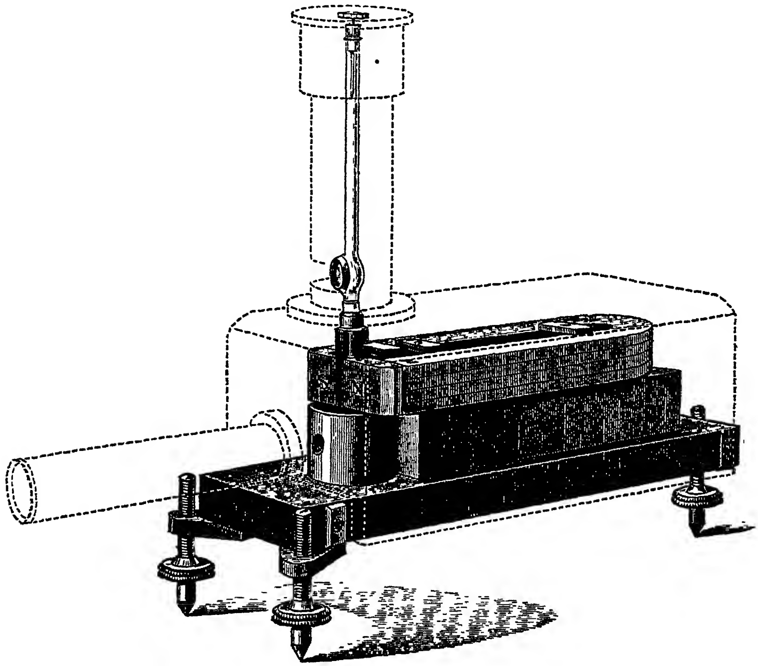


FIG. 136.

silk under varying conditions of temperature and humidity are obviated. The sensibility of the apparatus may also be varied at pleasure, and it may be rendered "dead beat," or its logarithmic decrement may be varied at will. A further advantage is that in spectroscopic work the radiation may be limited by a narrow slit without seriously reducing the sensibility of the instrument. On the other hand, it must, like the galvanometer, be kept in a fixed position, and cannot be handled or pointed in other than a horizontal direction, so that in this respect it is less convenient than thermopile or bolometer.

The radio-micrometer may be used differentially by placing a second couple in the upper end of the circuit, and this may be furnished with a separate window, so that the radiation from one source may fall on one couple, and the other may be exposed at the same time to the radiation from any other source.

Besides being vastly more sensitive than the thermopile, the radio-micrometer has a further advantage, which is most important in astronomical work, for a measure can be effected with it in a few seconds instead of the several minutes necessary to the older apparatus. So great was the delicacy of the apparatus constructed by Boys that the radiation received by the mirror of a telescope of 16 inches aperture from a candle situated at a distance of between 2 and 3 miles was distinctly observable, and an amount of heat of about $\frac{1}{1500000}$ of that received from the full moon could be detected with certainty. It was, therefore, legitimately hoped that this instrument would settle the question as to whether or not any radiation from the fixed stars had yet been perceived.

Stellar radiation.

Experiments in this direction had been made in 1869 by Huggins[1] with the thermopile; but although the results did not prove conclusively that the thermopile was capable of detecting such feeble radiation, yet they made it exceedingly probable that the effects observed were really due to stellar radiation. A year later Mr. Stone,[2] using the great equatorial at Greenwich and a single couple, found that at night every slight change in the sky, even though invisible to the eye, so disturbed the galvanometer that it was impossible to distinguish between effects due to the stars and those caused by the varying clearness of the sky. This difficulty was largely obviated by placing in the focal plane of the object-glass two thermo-electric pairs so connected that the heating of the exposed face of one would produce an effect opposite in kind to that produced by the heating of the exposed face of the other. Under these conditions a change in the sky affected the two faces equally or nearly so, and the galvanometer was not disturbed by variations of the sky; but if a star were allowed to shine first on one face and then on the other, corresponding deflections in opposite directions ought to be obtained. This arrangement had been employed previously by Lord Rosse[3] in his experiments on the heat of the moon. Mr. Stone concluded from his experiments that the radiation from Arcturus heated the face of the pile through about $\frac{1}{50}$ of a degree Fahrenheit! A quantity which

[1] Wm. Huggins, *Proc. Roy. Soc.*, vol. xvii. p. 309, 1869.

[2] E. J. Stone, *Proc. Roy. Soc.*, vol. xviii. p. 159, 1869.

[3] Lord Rosse, *Proc. Roy. Soc.*, vol. xvii. p. 436, 1869.

might be registered by any well-constructed liquid-in-glass thermometer.

With the radio-micrometer, however, which is vastly more sensitive than the thermopile, and which would detect with certainty a radiation enormously less than that of the full moon, Boys[1] could find no radiation effect from Arcturus or any other star or planet, and he has consequently proved that no heating effect from the stars has yet been observed.

251. Other Sensitive Radiometers.—A modification of the differential thermometer has been devised by Professor H. F. Weber,[2] of Zurich, which he calls a micro-radiometer, and for which he claims a delicacy that will detect one hundred-millionth of a degree. In this instrument the two bulbs of the differential thermometer are replaced by two thin boxes of brass, one end of each of which consists of a plate of rock-salt. These boxes are attached to the two ends of a narrow glass tube, the bore of which is about 1 sq. mm. in area. Near each end of this tube a small bulb is blown, and these bulbs and about 5 mm. of the tube at each end are filled with a solution of sulphate of zinc, which is prevented by capillary action from entering the boxes at the ends, and the middle of the tube (between the bulbs) is filled with mercury. Now if one box is warmed the liquid in the tube is driven towards the other, and this displacement is detected electrically by causing the 5 mm. or so of zinc sulphate at each end, between the small bulbs and the mercury, to form the two arms of a Wheatstone's bridge, the other two arms consisting of a pair of resistances, which are put into connection with the sulphate of zinc solution by wires sealed into the bulbs. Thus when any displacement occurs one column of the zinc sulphate is lengthened while the other is shortened, so that the resistance of one arm is increased while that of the other is diminished, and both causes conspire to disturb the equilibrium of the bridge. With this complex apparatus Weber states that the heat of the moon produced an oscillation of 100 scale divisions of the galvanometer. Micro-radiometer.

A delicate instrument for detecting thermal radiation has been constructed by Edison, and is named the Tasimeter. In this instrument the part of the apparatus exposed to radiation is a thin strip of vulcanite, which is supported between a screw at one end and a carbon resistance at the other, so that when it expands it presses against the carbon, and so diminishes the electrical resistance of the circuit. In describing this apparatus Professor Barrett[3] says: "The heat radiated from one finger held near the cone is more than sufficient to drive the galvanometer index right across and off the scale. In a letter relating to this tasimeter Mr. Edison writes to me as follows: 'By holding a lighted cigar several feet away I have thrown the light right off the scale, and by increasing the delicacy of the galvanometer the tasimeter may be made so sensitive that the heat from your body, while standing 8 feet from it and in a line with the cone, will throw the light off the scale, and the radiation from a gas-jet, 100 feet away, gives a sensible deflection.'" It thus appears that this instrument compares favourably in delicacy with the thermopile, but that it is far behind the radio-micrometer, either as a detecter or a trustworthy meter. Tasimeter.

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[1] C. V. Boys, *Proc. Roy. Soc.*, vol. xlvii. p. 480, 1890.

[2] Weber, *Archives de Genève*, 1887, p. 347. See Professor Boys's "Cantor Lectures," *Journal of the Society of Arts*, 20th September 1889.

[3] W. F. Barrett, *Telegraphic Journal*, 15th November 1878.

Michelson.

Professor A. A. Michelson[1] has also employed the large coefficient of expansion of vulcanite in the construction of a sensitive thermometer. In this instrument a very thin plate of vulcanite is gummed to an equal plate of copper, about 50 mm. long, 1 mm. broad, and 0·1 mm. thick. The lower extremity of this plate is fixed while the upper is gummed to a thin glass index, the end of which is bent at a right angle, and presses against a mirror suspended by a thread. When the temperature rises the double plate of copper and vulcanite curves, owing to the unequal dilatations of the two substances, and this motion is transmitted by the glass thread to the mirror whose deflection is noted by the motion of a spot of light on a scale. The form of the compound strip is rectangular, so that the instrument may be used in spectrum analysis; but if it is to be employed merely as a thermoscope, the strips may be rolled in the form of a helix after the manner of Bréguet's metallic thermometer, and the sensitiveness is thereby greatly increased. Besides its simplicity (a galvanometer not being required), the advantages claimed for this instrument are quick action, facility of regulation, and extreme sensitiveness.

Joule.

A sensitive thermoscope, depending in its indications on the air currents set up in an unequally heated compartment, was devised by Joule.[2] A glass tube, 2 feet long and 4 inches in diameter, is divided longitudinally into two compartments by a blackened pasteboard diaphragm, leaving spaces at the top and bottom about 1 inch wide, the diaphragm being about 2 inches shorter than the tube. In the space at the upper end a small magnetised sewing-needle, furnished with a glass index, is suspended by a silk thread. The tube is thus divided into two compartments by a plane through its axis, and if the temperature in one of these chambers is higher than in the other a flow of air takes place from the warmer to the colder above, and from the colder to the warmer below. The suspended needle is deflected by this current, and the sensitiveness of the apparatus becomes greater as the directive force of the needle is diminished. The heat of the moon's light was easily detected by means of this instrument.

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[1] Albert A. Michelson, *Journal de Physique*, tom. i. p. 183, 1882.

[2] Joule, *Proc. Manchester Lit. and Phil. Soc.*, vol. iii. p. 73.

CHAPTER VII

CONDUCTION

SECTION I

ON THE CONDUCTIVITY OF SOLIDS

252. Preliminary Considerations.—One of the three processes by which heat is transferred from one body to another, or from one part of a body to another, is termed conduction; the other two have been considered already, and are known as convection and radiation. In the case of radiation the propagation takes place with the velocity of light, and, except in the case of absorbing media, when radiant energy is transmitted through any body, it leaves the intermediate parts apparently unaffected.

The propagation of heat by conduction, on the other hand, is comparatively a very slow process, and the heat, in travelling through a body by this method, increases the temperature of the intermediate parts, and remains partly lodged in them, at least until a stationary condition is attained. When one end of a metal rod is placed in a lamp-flame, a gradual rise of temperature is noticed along the bar, the parts nearest the flame being warmer than those more remote. For some time the temperature at each point of the bar gradually increases, but ultimately a stationary condition is reached, and the temperature at each point remains permanently the same. In this stationary state, however, there is still a flow of heat along the rod, and the temperature has become steady, merely because the heat is radiated from the surface of the rod as fast as it is supplied at the end.

The process of conduction is usually regarded as essentially different from that of radiation, and it is sometimes described as the passage of heat from one body to another, or from one part of a body to another, "by contact," so that the heat passes from one layer to another while the matter remains at rest. This mode of passage might be intelligible if heat were regarded as a fluid, but from any other point of view it is without meaning. In the process of radiation heat is propagated as a free-wave motion in the ether, but in the process of conduction

the action of the matter through which the heat travels becomes of prime importance. Each molecule as it becomes heated may affect those around it, either by direct radiation or by forcing into vibration those with which it may come into contact. On consideration, therefore, it will appear that no entirely new process is essentially involved in the conduction of heat, but that all equalisation of temperature may be effected either by convection or by a process of intermolecular radiation and absorption.

Let us return to the molecular theory, and assimilate the molecules of a body to tuning-forks, or other vibrating systems, each having one or more definite periods of vibration, and, bearing in mind what has been already stated in Art. 228, let us consider the propagation of heat along a bar heated at one end. For greater clearness let us suppose that the end of the bar is heated by being placed very close to a hot radiating surface, such as a white-hot metal ball, and let the molecules of the bar be supposed free to vibrate independently—that is, spaced in the ether so that they may vibrate freely. The ball is then to be regarded merely as a source of waves in the ether, which, when emitted, fall upon the end of the bar. These waves are at first chiefly used up in setting in vibration a thin layer of molecules at the end of the bar. This layer (which we may say is a few millions of molecules deep) absorbs the waves at first almost completely, and protects those behind from disturbance. Very soon, however, the front molecules are set in active vibration, and become sources of disturbance themselves, radiating waves in the ether, so that new molecules in the rear begin to be set in motion, and the disturbance is thus gradually propagated along the bar by a process of absorption and subsequent radiation (by the molecules) of the waves from the source of heat.

So far we have no contact considerations whatever, the whole process is simply the propagation of wave motion through an absorbing system. Of course the molecules may be in contact, at least some of them may, and jangling may take place, so that when one molecule is disturbed it forces the vibrations of others close to it. The supposition of actual contact is, however, not absolutely necessary to the intelligible explanation of the phenomenon, as will perhaps be more clear from the following illustration.

Let us suppose that a vast number of boats are moored in a large harbour, and let each boat floating on the water correspond to a molecule of matter in the ether. Now let a storm arise at some distance out at sea, and let the waves travelling to shore approach the harbour, and be of such a period that the boats absorb them and

are thus set vibrating. The first waves which arrive will be almost entirely absorbed by the front row of boats, so that those nearer land are quite protected from disturbance. After a little, however, the front ranks are in violent oscillation, and cease to absorb any sensible fraction of the waves which fall upon them; or, regarded from the other point of view, they radiate as much as they absorb. The waves are now able to penetrate farther, and gradually reach the boats in the rear, so that the disturbance is thus gradually *conducted* through the whole system.

The propagation of a disturbance in this manner would be expected to be a fairly slow process, such as we actually observe in nature, the rate of propagation being determined by the rate at which the waves are absorbed by the molecules and by the molecular capacities —that is, by the whole period of absorption of any molecule, or the interval of time between the commencement of absorption by a molecule, and the stage at which it radiates as much as it absorbs. This interval will, of course, depend on the nature of the molecules, and the conductivity may be expected to vary considerably in different substances.[1] The simplest experiments show us that different bodies vary enormously in conducting powers. For example, a silver spoon placed in a cup of hot tea soon becomes heated throughout its length, while a glass rod placed in the same cup will scarcely ever show any perceptible increase of temperature at its farther end; but although we have substances like glass which are bad conductors of heat, yet we have no non-conductors of heat as we have non-conductors of electricity. This is a serious disadvantage, and is much felt in almost every department of practical life.

Comparison of Conductivities

253. Ingen-Hausz's Experiment.—One of the earliest methods of *comparing* the conductivities of different bodies for heat was suggested by Franklin, and the comparison was carried out by Ingen-Hausz.[2] Bars of the various substances were prepared and coated with bees'-wax. Their ends were then immersed in a bath A of hot oil

[1] Pictet supposed that heat ascends in a solid more rapidly than it descends, but the observations which led him to this opinion were probably influenced in a considerable degree by upward air currents. For even in the so-called vacuum of an air pump sufficient air remains to explain his experiments. Ascending currents are produced in the neighbourhood of the hot body, and for this reason cold air continually approaches its lower parts, so that the heat is carried upwards.

[2] Ingen-Hausz (Jean): "Sur les métaux comme conducteurs de la chaleur," *Journ. de Phys.*, tom. xxxiv. pp. 68, 380; 1789.

(Fig. 137), and after standing some time it was observed that the wax was melted off the different bars to different lengths. On some of the bars the wax is melted off more rapidly, and on some to greater distances, than on others, but it does not hold that those from which the wax is melted most rapidly at first are those from which it will be furthest melted on prolonged immersion. If all the bars had the same conducting power—that is, allowed the same flow of heat per unit time—then when the wax is melting the temperature at any point of the bar will be less the greater the specific heat, so that on those of the lowest specific heat the wax will melt most rapidly; but on prolonged immersion the temperature of the bar reaches a permanent state, and all the heat which enters it by conduction leaves it by radiation.

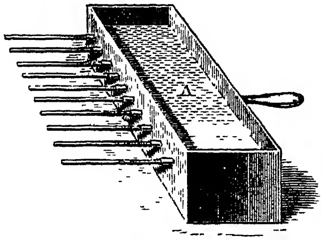

Fig. 137.—Ingen-Hausz's Experiment.

It has been demonstrated by Professor Tyndall that the temperature wave travels faster in bismuth than in iron, though the conductivity of bismuth is much less than that of iron. The specific heat becomes of no account when the stationary state is attained, and the length of wax melted will be greater as the conductivity is greater. The length melted off when the permanent state is arrived at will not, however, be in the simple ratio of the conductivities, but if the bars have the same cross-section and the same coefficients of emission, we shall show further on that the conductivities k and k' of any two on which the lengths ultimately melted off are l and l' are related by the equation

$$\frac{k}{k'} = \frac{l^2}{l'^2}.$$

To secure the same coefficient of emission the bars may be electroplated and polished. The rate of melting of the wax on any bar measures the rate at which a wave of temperature travels along it, but this is not the conductivity. The relative conductivities are determined alone from the lengths melted off when the *permanent stage* is arrived at.

Another form of the experiment consists in attaching small pellets to the lower sides of the bars by means of wax. The temperature at which the wax is sufficiently softened to allow the pellets to fall off travels along the bars at different rates, but if the balls be equally spaced the conductivities will be as the squares of the numbers of balls melted off when the permanent state is attained.

RECTILINEAR FLOW OF HEAT—CONDUCTION THROUGH AN INFINITE WALL

254. Precise Definition of Conductivity.—The first to give a thoroughly scientific definition of conducting power was Fourier, who, in his *Théorie Analytique de la chaleur* (1822), treated the subject of the propagation of heat with a power and completeness which left little room for extension or improvement, and suggested or rendered possible almost all later developments.[1]

In order to obtain an exact notion of conduction, let us consider the case of a plane lamina or wall, with parallel faces, one of which is kept at a fixed temperature θ_1, while the other is maintained at θ_2. Here there will be established a permanent state and a uniform flow of heat from the hotter to the colder face, and the temperature may be taken to fall uniformly from θ_1 at one face to θ_2 at the other, if the wall be throughout of the same material, and if the conducting power does not depend on the temperature. Hence, if we consider any plane drawn in the wall parallel to the faces, it is clear that the same quantity of heat will pass across every such plane per second when the permanent state is established.

In estimating this quantity of heat the first principle that we make use of is, that the quantity of heat which flows through such a wall is directly proportional to the difference of temperature $(\theta_1 - \theta_2)$ of its faces. This we may regard as established by experiment. From this it will follow that for walls of the same substance and of different thicknesses, whose faces have the same temperature difference $(\theta_1 - \theta_2)$, the flow will be in the inverse ratio of the thickness. For since the difference of temperature between the faces is the same for all the walls, then the fall per unit thickness is inversely as the thickness, and consequently the flow through a plate of unit thickness of any wall, which is the same as the flow through the wall, will be inversely as the thickness of the wall. Further, the quantity of heat which flows through an area A of such a wall in a time t will be proportional to A and also to t. We consequently have for the quantity which flows through a plate of area A and thickness e in a time t—

$$Q = K\frac{\theta_1 - \theta_2}{e}At.$$

[1] With respect to Fourier's work, Professor Tait says: "Its exquisitely original methods have been the source of inspiration of some of the greatest mathematicians; and the mere application of one of its simplest portions to the conduction of electricity has made the name of Ohm famous."

The coefficient K is a quantity depending on the nature of the substance, and is called the *conductivity* of the substance. Taking the case of a wall of unit thickness, with unit difference of temperature between its faces, we find that the conductivity *K is numerically equal to the quantity of heat which flows per unit time through unit area of a plate of unit thickness, having unit difference of temperature between its faces.*

If we suppose the lamina to have an infinitely small thickness dx and an infinitely small temperature difference $d\theta$ between its faces, the quantity of heat which flows through it in a small time dt will be

$$Q = KA\frac{\theta-(\theta+d\theta)}{dx} = -KA\frac{d\theta}{dx}dt.$$

The quantity $d\theta/dx$ is the *gradient of temperature* at any point—that is, the change of temperature per unit thickness—and the above expression for Q, which is of fundamental importance in the theory of

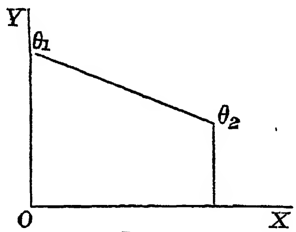

Fig. 138.

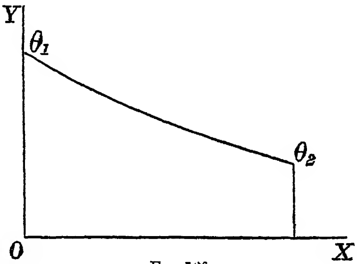

Fig. 139.

conduction, expresses that the flow through unit area per unit time is equal to the conductivity K multiplied by the temperature gradient.

We have so far considered the substance homogeneous—that is, that each layer of the wall possesses the same conducting power, so that the temperature falls uniformly from one face to the other, and the temperature gradient is uniform. The curve representing the relation between the temperature θ at any point and the distance x of the point from one face will therefore be a right line (Fig. 138)—

$$\theta = a + bx.$$

The constants a and b are easily determined, for when $x=0$ we have $\theta=\theta_1$, therefore $a=\theta_1$; and when $x=e$ we have $\theta=\theta_2$, therefore $\theta_2=\theta_1+be$ or $b=(\theta_2-\theta_1)/e$. The temperature at any point of the wall is consequently

$$\theta = \theta_1 - \frac{\theta_1-\theta_2}{e}x.$$

If, however, the various layers of the wall have different conductivities the temperature gradient will not be uniform, and the relation between

θ and x will not be linear. When the conductivity is good the slope of temperature will be small, but the reverse will hold when the conductivity is bad. Fig. 139 would represent the temperature curve for a wall in which the conductivity gradually improved from the face θ_1 to the face θ_2. Something like this may actually hold in nature, for the quantity K, instead of being a constant for a given kind of matter, will in general depend upon its physical state as regards temperature and pressure. We know that electrical conductivity diminishes as the temperature rises, but the evidence as to thermal conductivity is not yet sufficiently accurate or extended. In general, those substances which are the best conductors of electricity are also the best conductors of heat, and anything which affects one may also influence the other. In the case of the wall considered above, the temperatures of the layers near the face θ_1 are higher than those near the face θ_2; consequently, if the conductivity at high is less than at low temperatures, the slope of temperature will be steeper near the face θ_1 than near the face θ_2.

In all such cases, however, when the steady state is established, the quantity of heat which passes each layer is the same, and we have therefore

$$\mathrm{K}\frac{d\theta}{dx}=\text{constant}.$$

Hence if K be given as a function of x and θ, the above differential equation determines the form of the temperature curve and the gradient at each point of the wall.

Ex. 1. If K varies as θ, then—

$$\theta^2=ax+b,$$

and the temperature curve is consequently a parabola.

Ex. 2. If K varies inversely as x, we have

$$\theta=ax^2+b,$$

and the temperature curve is again a parabola.

Ex. 3. If K is proportional to x, we have

$$\theta=a\int\frac{dx}{x}=a\log x+b,$$

or

$$x=\mathrm{A}e^{\frac{\theta}{a}},$$

and the temperature curve is consequently logarithmic.

255. Steady Flow of Heat through a Long Bar.—Let us now consider the case of a long bar heated steadily at one end. For some time after the first application of heat at the end the temperature at each point of the bar will gradually rise, but ultimately each point will acquire a stationary temperature and a steady flow will take place

along the bar. Theoretically it would require an infinite time to reach this steady state, but it is practically attained in a comparatively short time, depending on the nature of the bar. Supposing this stage to have been attained, let θ be the temperature of the surface at a distance x from the hot end, measured along the axis of the bar. Then if we suppose the temperature gradient to be uniform over the cross-section A of the bar at this point, or if its mean value over the section be $d\theta/dx$, the flow of heat per unit time across this section will be

$$-\mathrm{KA}\frac{d\theta}{dx}.$$

But the temperature at an adjacent point, $x+\delta x$, will be $\theta+\frac{d\theta}{dx}\delta x$, since $d\theta/dx$ is the rate at which the temperature rises along the bar, and this multiplied by δx will be the rise of temperature in passing from the point x to $x+\delta x$, if δx be taken so small that the temperature gradient is sensibly constant between the two points. Hence the flow of heat across the section at the point $x+\delta x$ will be

$$-\mathrm{KA}\frac{d}{dx}\left(\theta+\frac{d\theta}{dx}\delta x\right),$$

and consequently the excess of what flows in at one face of the element over what flows out at the other will be

$$\mathrm{KA}\frac{d^2\theta}{dx^2}\delta x.$$

Now, in the steady state this excess must be entirely radiated from the surface of the element, and denoting the perimeter of the bar by p, the area of this surface is $p\delta x$, so that if θ be measured from the temperature of the surrounding medium—that is, if θ is the excess of the temperature of the surface of the element over that of the surrounding medium, the heat radiated by the element will be $\mathrm{E}p\theta\delta x$, assuming Newton's law, where E is the surface emissivity of the bar. Hence in the steady state we have [1]

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[1] This equation may also be written in the form

$$k\frac{d^2\theta}{dx^2}=-\frac{d\theta}{dt},$$

where $-d\theta/dt$ is what Forbes termed the statical rate of cooling—that is, the rate at which the element would cool if isolated from the rest of the bar, and $k=\mathrm{K}/c$, where c is the thermal capacity of the substance per unit volume. For if we consider the element isolated and to lose heat by its surface $p\delta x$ only, then the rate of loss is, by Newton's law, $\mathrm{E}p\theta\delta x$, but this must be counterbalanced by a fall of temperature, so that if the rate of fall of temperature of the element be $-d\theta/dt$, we have

$$\mathrm{E}p\theta\delta x=-c\mathrm{A}\delta x\frac{d\theta}{dt}:$$

$$KA\frac{d^2\theta}{dx^2}=Ep\theta,$$

or

$$\frac{d^2\theta}{dx^2}=\mu^2\theta,$$

where for brevity we have written

$$\mu^2=\frac{Ep}{KA}.$$

It may be easily verified by substitution that the solution of this equation is

$$\theta=Me^{\mu x}+Ne^{-\mu x},$$

where M and N are constants to be determined by the conditions of the problem.

COR. *Ingen-Hausz's Experiment.*—In this case the wax is melted off a bar to a distance l, and the temperature here is the melting-point of the wax. We also suppose that the bars are very long, so that their extremities are at the temperature of the surrounding medium; in this case we have the excess $\theta=0$, when $x=\infty$, therefore

$$0=Me^{\mu\infty}+Ne^{-\mu\infty}=Me^{\mu\infty},$$

consequently

$$M=0.$$

But when $x=0$ the excess of temperature is that of the source θ_0, therefore

$$\theta_0=N,$$

and therefore we have in general for the excess of temperature θ, at any distance x,

$$\theta=\theta_0 e^{-\mu x}.$$

Now if on any bar a length l_1 of the wax is melted off, we have

$$\theta_1=\theta_0 e^{-\mu l_1},$$

where θ_1 is the melting-point of the wax, measured from the temperature of the surrounding medium, and hence

$$\mu l_1=\log\left(\frac{\theta_0}{\theta_1}\right).$$

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so that

$$\frac{Ep}{A}\theta=-c\frac{d\theta}{dt},$$

therefore, etc.—See further, *Phil. Mag.*, March 1879, pp. 198, 251, Dr. O. J. Lodge.

Now for all the bars θ_1 and θ_0 are the same, therefore if the wax is melted off to distances l_1, l_2, l_3, etc., we have

$$\mu_1 l_1 = \mu_2 l_2 = \mu_3 l_3 = \ . \ . \ . \ \text{constant.}$$

For any two bars we have consequently

$$\frac{l_1}{l_2} = \frac{\mu_2}{\mu_1},$$

or

$$\frac{l_1^2}{l_2^2} = \frac{E_2 p_2}{K_2 A_2} \div \frac{E_1 p_1}{K_1 A_1}.$$

Hence if the bars have the same cross-section, perimeter, and coefficient of emission, we shall have

$$\frac{K_1}{K_2} = \frac{l_1^2}{l_2^2},$$

or

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \text{etc.}$$

256. Comparison of Conductivities by Means of Three Temperatures at Equal Distances.—Let the temperatures of the bar (Fig. 140) at distances x, $x + a$, $x + 2a$, be θ_1, θ_2, θ_3, then we have

$$\theta_1 = Me^{\mu x} + Ne^{-\mu x} = a + b, \text{ suppose.}$$
$$\theta_2 = Me^{\mu(x+a)} + Ne^{-\mu(x+a)} = ae^{\mu a} + be^{-\mu a}.$$
$$\theta_3 = Me^{\mu(x+2a)} + Ne^{-\mu(x+2a)} = ae^{2\mu a} + be^{-2\mu a}.$$

Eliminating a and b from these equations we have

$$\begin{vmatrix} \theta_1 & \theta_2 & \theta_3 \\ 1 & e^{\mu a} & e^{2\mu a} \\ 1 & e^{-\mu a} & e^{-2\mu a} \end{vmatrix} = 0,$$

or

$$\theta_1(e^{\mu a} - e^{-\mu a}) - \theta_2(e^{2\mu a} - e^{-2\mu a}) + \theta_3(e^{\mu a} - e^{-\mu a}) = 0.$$

Dividing by $e^{\mu a} - e^{-\mu a}$ we have

$$\theta_1 - \theta_2(e^{\mu a} + e^{-\mu a}) + \theta_3 = 0,$$

that is

$$e^{2\mu a} - \frac{\theta_1 + \theta_3}{\theta_2} e^{\mu a} + 1 = 0.$$

Denoting $\dfrac{\theta_1 + \theta_3}{\theta_2}$ by $2n$ we have the quadratic

$$e^{2\mu a} - 2ne^{\mu a} + 1 = 0,$$

or

$$e^{\mu a} = n + \sqrt{n^2 - 1},$$

the positive sign being taken with the radical, because in the experiment of Art. 257, $\theta_1 + \theta_3$ is greater than $2\theta_2$, therefore n lies between

one and two. But $e^{\mu a}$ is greater than unity, and $n - \sqrt{n^2 - 1}$ is less than unity. Hence we have finally

$$\mu a = \log (n + \sqrt{n^2 - 1}),$$

and for two bars of the same perimeter, section, and coefficient of emission we have, taking a the same in both—

$$\sqrt{\frac{K_1}{K_2}} = \frac{\mu_2}{\mu_1} = \frac{\log (n_2 + \sqrt{n_2^2 - 1})}{\log (n_1 + \sqrt{n_1^2 - 1})}.$$

Hence,[1] by reading the temperatures of three thermometers placed at equal distances from each other in bars of various substances, their conductivities may be compared—that is, the specific or relative conduc-

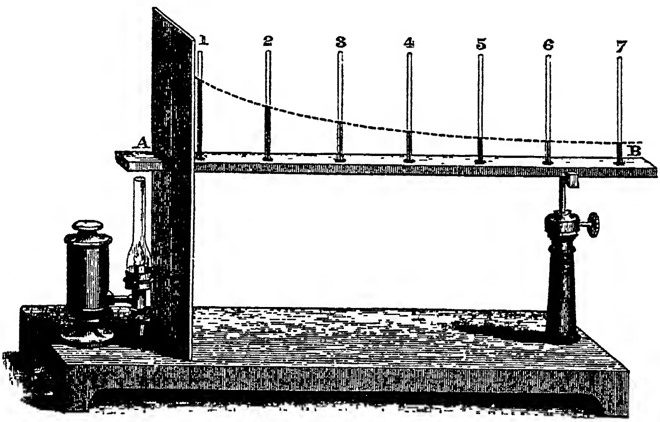

Fig. 140.

tivity of any bar may be obtained, but the absolute conductivity as defined in Art. 254 remains still unknown.

257. Despretz's Experiments.—The principles of the foregoing article were made use of by Despretz[2] in a series of experiments on the relative conductivities of bars of various metals. The bar under experiment was heated at one end by a steady lamp, and the temperatures at various points of the bar were determined by means of thermometers which were inserted in small holes sunk into the axis of the bar (Fig. 140). The thermometers are brought into intimate contact with the bar by having their bulbs surrounded by a little

[1] This equation suggests a method of comparing the emissivities of the surface of a bar when coated with different substances, or when in different states of polish. For when n_1 and n_2 are determined for the same bar in two different surface conditions, we know the ratio of μ_1 to μ_2—that is, of E_1 to E_2.

[2] Despretz, *Ann. de Chimie et de Physique*, 2e, tom. xix. p. 97, 1822; and tom. xxxvi. p. 422, 1827.

mercury, or in the case of high temperatures by a fusible alloy, placed in the holes into which they are inserted. By this means the temperature curve along the entire length of the bar can be plotted, and this curve, if the principles assumed in Art. 255 are accurately fulfilled, should be logarithmic. The conditions assumed in the theory are, however, only approximately fulfilled in practice, and the curve is found on trial to be only approximately logarithmic. The logarithmic curve between any two points is found to lie above the experimental curve, so that the latter has a greater sag towards the bar than the former.

In order to compare the conductivities of two bars by the method of the foregoing article it is necessary that they should have the same surface emissivity, and this may be secured, at least approximately, by coating them with lamp-black, or a black varnish, or by electroplating, or more simply by covering them with white paper pasted on. If, in addition, the cross-sections and perimeters of the bars under comparison be the same, the conductivities of any pair are compared by the formula

$$\sqrt{\frac{K_1}{K_2}}=\frac{\log(n_2+\sqrt{n_2^2-1})}{\log(n_1+\sqrt{n_1^2-1})},$$

where, if θ_1, θ_2, θ_3 are the temperature excesses registered by three equidistant thermometers, then $2n=(\theta_1+\theta_3)/\theta_2$. Despretz verified the theoretic deduction of the foregoing article, viz. that the temperature excesses of a series of equidistant thermometers along the same bar were related, by the equations

$$\frac{\theta_1+\theta_3}{\theta_2}=\frac{\theta_2+\theta_4}{\theta_3}=\frac{\theta_3+\theta_5}{\theta_4}=\text{etc.}$$

Objections have been raised to this method of experiment on the ground that the thermometer holes sunk in the bar introduce a discontinuity into the material, which alters both the distribution of temperature and the flow of heat. The error introduced in this manner will, however, be inappreciable if the widths of the cavities be fairly small compared with the diameter of the bar. For example, a cavity 2 mm. wide cannot produce any sensible effect on the flow of heat through a bar from 1 to 2 centimetres thick, especially when the cavities are filled up with a fluid metal.

In order to secure the same surface emissivity Despretz coated the bars with lamp-black, but this so increased the emissivity that the temperature fell very rapidly along the bar, and in many cases it became very difficult to observe the difference of temperature between two thermometers even at a short distance from the heated end.

Any want of homogeneity in the bars will also introduce considerable difficulty and uncertainty into such experiments as these, and perfectly homogeneous bars, free from all impurities, are perhaps not to be obtained. For such reasons, therefore, differences are to be expected between the results obtained by different observers from experiments made on different specimens of the same substance, and discrepancies of a more or less serious aspect are not surprising.

258. **Experiments of Wiedemann and Franz.**—In order to examine the accuracy of the results obtained by Despretz a new series of experiments was undertaken by Wiedemann and Franz.[1] The principle of the method adopted was the same as that of Despretz, but the apparatus employed differed in some important respects. The bars employed were about half a metre long and 6 mm. in diameter,

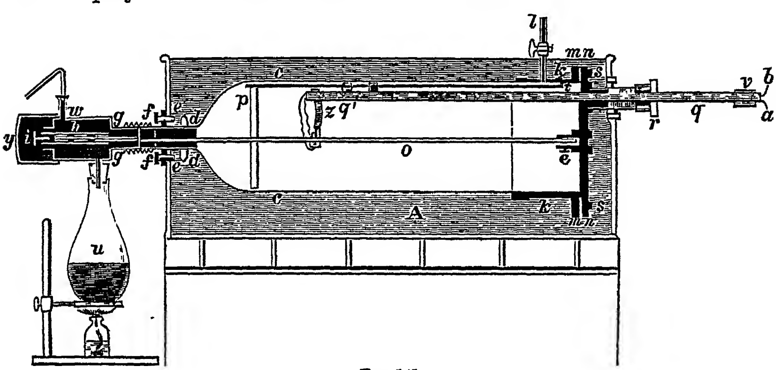

Fig. 141.

and in order to secure the same surface emissivity they were electroplated.

The bar under examination was fixed horizontally in the centre of a glass vessel (Fig. 141) which was air-tight, and could be exhausted so that experiments could be made in a vacuum as well as in air. This vessel was immersed in a water-bath, the temperature of which could be determined and kept constant. The end of the bar was heated by a current of steam, and its temperature was thus kept approximately at 100° C. The temperatures at various points along the bar were determined by means of a thermopile, the leading wires of which passed through a glass tube which could be protruded into the interior of the inner vessel at will, so that the pile could slide along the bar and register the temperature at its various points. The pile was graduated by direct experiments made by heating, within the apparatus itself, a hollow tube of steel filled with mercury and containing a thermo-

[1] Wiedemann and Franz, *Ann. de Chimie*, 3^e, tom. xli. p. 107, 1854.

meter.[1] The results of these experiments are contained in the following table :—

RELATIVE CONDUCTIVITIES

	In Air.	In Vacuum.
Silver	100	100
Copper	73·6	74·8
Gold	53·2	54·8
Brass	23·1 24·1	25·0 24·0
Tin	14·5	15·4
Iron	11·9	10·1
Steel	11·6	10·3
Lead	8·5	7·9
Platinum	6·3	7·3
Rose's alloy	2·8	2·8
Bismuth	1·8	...

259. On the Experimental Determination of Absolute Conductivities.—The definition of conductivity stated in Art. 254 suggests at once a method of estimating it in absolute measure, for if the two faces of a plate of known thickness and area be maintained at fixed temperatures, and if the difference of these be accurately known, as well as the quantity of heat which flows through the plate per second, then all the quantities necessary for the estimation of K will be known. Thus, if steam be blown against one face of the plate, and if melting ice or water be placed in contact with the other, the flow of heat may be ascertained by the amount of steam condensed on one side, or by the amount of ice melted on the other, or by the change of temperature of the water.

A great difficulty attending this method arises, however, in the determination of the exact temperatures of the faces of the plate, for the hot face is certainly colder than the vapour, and the cold face is undoubtedly warmer than the water or ice in contact with it. The difference of temperature between the faces of the plate will therefore be much less than the difference of temperature between the steam on

[1] Langberg (*Pogg. Ann.*, B. lxxxix. p. 1, Sept. 1853) introduced the method of thermoelectric couples instead of the thermometers used by Despretz. The junction was applied against the bar. Wiedemann and Franz employed the same method, but adopted many precautions neglected by Langberg. The principal objection to Langberg's work is the neglect of making the same closeness of contact with the couple in all cases, and in employing wires instead of bars the errors due to air-currents and accidental causes were greatly magnified. The possibility of a definite difference of temperature between the bar and the junction is a serious objection raised by Verdet.

one side and the water on the other. To proceed on the supposition that the hot face is at the temperature of the steam, or very approximately so, and that the cold face is also very nearly at the temperature of the melting ice or water, is to assume conditions which are very far from the truth. This is shown clearly by the results obtained in this manner by Clément and Péclet.[1] The number obtained by the former for the conductivity of copper being about 200 times too small, and that of the latter 6 times too small.[2] This means that, if the other quantities be supposed to have been correctly observed, the difference of temperature between the faces of the plate was with the former 200 times and with the latter 6 times less than was supposed.

The change of temperature in passing through a thin film of water in contact with the plate may, in such an experiment, be much greater than the whole difference between the faces of the plate, so that although the face of the plate is essentially at the same temperature as the surface of the adjacent film, yet it may differ largely from the temperature registered by any ordinary thermometer placed close to it, nor does it seem likely that the difficulty could be quite got rid of by taking the temperature of the face by means of thermoelectric junctions. Péclet seems to have been alive to this source of error in Clément's experiments, for he vastly improved his apparatus by placing a special stirrer in the water so that fresh layers were constantly brought into contact with the face of the metal plate; but even this only partially removed the error, for the surface film adheres to the plate, and no process of stirring would remove it with sufficient rapidity to keep the face of the plate at anything like the mean temperature of the liquid.

The only hopeful method then is to take temperatures in the metal itself and not outside it. Thus, if the plane faces of the plate be supposed vertical, then small vertical holes should be drilled in the plate, one near each face, and the temperatures of the metal at these points may be taken either by small thermometers placed in the holes or by some thermoelectric method. By this means the temperatures of the two faces of a layer of known thickness of the plate are known, and all the quantities required for the determination of K may be obtained with tolerable accuracy. This amounts practically to what we shall describe as the guard-ring method.

Another method was devised by Forbes in 1850, and although it is very simple in principle, yet it is exceedingly tedious and laborious in practice. The object of the method is to determine K by estimating

[1] Péclet, *Ann. de Chimie et de Physique*, 3^{e}, tom. ii. p. 107, 1841.

[2] See Art. "Heat," *Ency. Brit.* (Lord Kelvin).

the quantity of heat that flows through any section of a bar, heated at one end, as in the experiments of Despretz. When the stationary stage is attained, the whole heat that crosses any section of the bar is radiated from the surface between the section and the cool end of the bar. If, therefore, the temperatures be known at all points along the bar, and if the emissivity of the surface be also determined for all temperatures by separate observations on a similar bar, or on part of the same bar, then the whole quantity of heat radiated per second by the surface between any cross-section and the cold end can be calculated. This with the temperature gradient at the section in question gives the conductivity. The temperature gradient is found from the temperature curve, being the trigonometrical tangent of the angle which the tangent line at the corresponding point of the curve makes with the axis of x. Hence when the temperature curve is plotted, we can find the temperature gradient at any point of the bar.

A third method has also been devised and employed with success. This method was introduced by Ångström and depends on the observation of the periodic flow of heat in a bar alternately heated and cooled at one end or at some point of its length. We shall consider this method fully later on; at present we shall describe the experiments of Forbes, as they were the first to yield trustworthy results.

260. Forbes's Method.—As already mentioned, the experimental method of Forbes[1] consists essentially of two distinct observations—one, the determination of the temperature curve, and thence the estimation of the temperature gradient at all points along a bar heated steadily at one end, and the other the determination of the rate of cooling of a similar bar uniformly heated, and then left to cool in the open air under the same conditions as the first bar. The first was termed by Forbes the *statical*, and the second the *dynamical*, or cooling, experiment. In the former the observations are made on a bar when the steady state has been acquired, and it is steady temperatures that are taken, whereas in the latter the observations are made on the rate of cooling of a bar, and the temperatures registered are those of a cooling body. The two bars may therefore be referred to, for brevity, as the *statical* and *dynamical* bars respectively.

The Statical Experiment.—In this experiment a bar of wrought iron 8 feet long and $1\frac{1}{4}$ inch square section was used. One end was heated by being fixed into a cast-iron crucible, which was finely adjusted to it,

[1] Forbes, James D., *Phil. Trans. Roy. Soc.*, Edinburgh, vol. xxiii. p. 133, April 1862. The experiments described in this paper were made ten years previous to its publication, and a brief account of them was communicated to the British Association at Belfast in 1852.

and contained molten lead or solder. This was kept in the fluid state and at as uniform a temperature as possible by means of a powerful gas furnace. By adjusting the gas-flame, and by placing pieces of the solid metal in the fluid, the temperature of the heated end could be regulated with considerable exactness, and kept constantly at the melting point of lead or solder. This, however, was a very laborious process, as the experiment lasted from six to eight or even ten hours. The iron bar was so long that the temperature of the farther end was not sensibly raised during the experiment, and it was employed in two surface conditions—one in which the surface was bright, and the other in which it was covered with thin white paper,[1] applied with the least possible quantity of paste, so that the conductivity of the same bar might be determined when the surface emissivity was greatly changed (in the ratio 1: 8, according to Leslie).

The temperature curve was determined by means of ten thermometers placed in small holes (0·28 inch diameter) drilled in the bar. The holes in the colder part of the bar were filled with mercury, while those near the hot end were filled with a fusible metal in a semifluid state, as it was found that when mercury was used in the warmer holes the surface became hotter, by convection, than the central part of the hole, contrary to the law of distribution of heat in a solid bar, and consequently an undue (though perhaps hardly sensible) amount of heat was thereby dissipated. It was also ascertained by direct experiment that the boring of several additional holes between the extreme holes did not sensibly disturb the flow of heat when the intermediate holes had thermometers surrounded by mercury inserted in them.

The temperature curve must be determined by readings of all the thermometers in the steady state, and this is extremely difficult to secure in practice, for the instant has to be seized when the casual fluctuations become inappreciable simultaneously on all the thermometers, and although the source of heat may appear quite steady for a time, yet the temperature wave arising from some antecedent irregularity may still be travelling along some more remote portion of the bar. Experience, and the patient entry of a number of successive observations of all the thermometers, can alone secure the desired precision.[2]

[1] The paper might also be used to render the surfaces of different bars alike, and for this purpose it would no doubt be much better than a black varnish, the difficulties arising from the use of which have been already noticed as a source of considerable trouble to Despretz.

[2] One good thermometer might be used to take all the readings by the *stepping method*, and the necessity of having a large number of accurate thermometers may

The Dynamical Experiment.—The dynamical or cooling experiment was made on an iron bar in all respects similar to that employed in the statical experiment, except that it was only about 20 inches long. A small hole was bored at the centre of one side (Fig. 142) in which a thermometer could be placed with an amalgam round it as in the previous experiment. At first a high uniform temperature was communicated to this bar by immersing it in a cylindrical vessel containing a heated fusible metal (4 parts lead + 3 tin + 3 bismuth). The bar was first wrapped in several folds of paper to prevent any sudden chill of the fluid metal on its first immersion, and it was completely immersed and withdrawn a few times, each end being alternately lowest, so as to equalise its temperature as much as possible throughout. When thoroughly heated it was withdrawn, and the paper cover was rapidly cut off. The naked bar was then placed horizontally on two blunt-edged props, so as to cool under the same circumstances as the statical bar. Mercury, previously heated, was placed in the hole, or holes (there were usually two or three near the centre of the bar), and thermometers were inserted. The temperatures were then read off from minute to minute, and the rate of cooling determined, the object of the experiment being to determine the rate at which any element of surface of the statical bar loses heat, ascertained in terms of the temperature registered by a thermometer sunk in the bar at that point.[1]

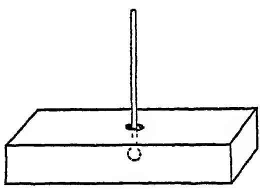

Fig. 142.

Calculation of the Flux of Heat.—From the results of these two

be thus avoided. For if a single accurate thermometer be possessed, it may be placed at first in the hottest hole, and then in the others successively, after being allowed to cool, until it has very approximately attained the temperatures of the thermometers in the other holes in succession. All the readings may be thus made with one good thermometer.

It is also worthy of note that the form of the temperature curve may be sensibly influenced by convection currents.

[1] At temperatures approaching 200° C. a difficulty arose which could not be completely overcome. When a bar has been heated uniformly the distribution of heat over any cross-section is not the same as when the bar in the statical experiment has attained the permanent state, nor is it the same as when the bar under experiment has cooled to a certain extent. In fact, it has been shown by Fourier that in the early stages of cooling of a body which has been uniformly heated, the expression for the temperature at any point includes certain circular functions which, in the case of good conductors, rapidly become evanescent. Such oscillations of temperature affect the rate of cooling, and are perceptible in the higher part of the scale, their general tendency being to make the rate of cooling of a thermometer sunk in the axis of the bar at first too small, for the bar is at first only superficially cooled. These irregularities at temperatures approaching 200° C. are mentioned by Forbes as the greatest difficulty met with in the inquiry.

experiments the flow of heat across any section of the statical bar may be evaluated in the steady state. The temperature curve being plotted, tangents were drawn at its various points, and the ordinates MP (Fig. 143) and subtangents MN measured. The ratio of these gave the value of $d\theta/dx$, the temperature gradient at each point along the bar. The results derived from the dynamical experiment were also represented graphically, the temperatures being taken as ordinates, and the corresponding times as the abscissæ of a curve. Tangents were drawn to this curve, and the corresponding subtangents measured. The ratio of these at any point of the curve gave the rate of cooling $d\theta/dt$ at the corresponding temperature. These rates having been tabulated, another curve was constructed, having the rates of cooling for ordinates, and the corresponding lengths along the statical bar for abscissæ. The ordinate of this curve (Fig. 144) being $d\theta/dt$, it follows that the element of area between two very close ordinates at a distance dx will be proportional to the quantity of heat radiated by the element per second, and hence the area of this curve between the ordinate corresponding to the point x and infinity (the cold end of the bar) represents the total loss of heat from the surface of the bar beyond the section; or, in other words, the flow of heat across this section. This curve is approximately logarithmic, and the area between any two ordinates can be calculated with sufficient exactness.

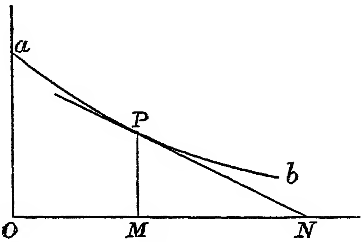

Fig. 143

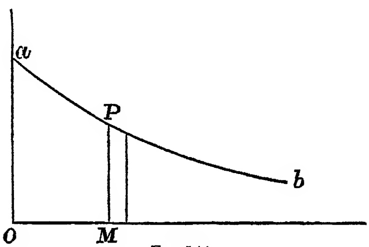

Fig. 144.

The following table contains the results of the experiments :—

[TABLE

NAKED BAR.				
Temperature.	Excess above Air.	$\frac{d\theta}{dx}$	Flux Q.	$Q/\frac{d\theta}{dx} \propto K$.
°C.	°C.			
25	12	11	0·15	0·0136
50	37	40	0·52	0·0130
75	62	71	0·93	0·0131
100	87	104	1·31	0·0126
125	112	142	1·71	0·0122
150	137	187	2·08	0·0112
175	162	244	2·43	0·0100
200	187	310	2·72	0·00875
COVERED BAR.				
25	12	15	0·22	0·0147
50	37	52	0·72	0·0138
75	62	92	1·13	0·0123
100	87	138	1·56	0·0113
125	112	187	2 00	0·0107
150	137	235	2·45	0·0107
175	162	295	3·00	0·0102

In order to express K we must multiply the numbers in the final column by the product of the specific heat and specific gravity of iron. This product was taken as 0·888, and the numbers for the conductivity of wrought iron become—

CONDUCTIVITY OF WROUGHT IRON ($1\frac{1}{4}$-INCH BAR)

Temperature.	Foot, Minute, and Centigrade Degree Units.	Centimetre, Minute, and Centigrade Degree Units.
°		
0	0·0133	12·36
25	0·0127	11·80
50	0·0120	11·15
75	0·0114	10·59
100	0·0107	9·94
125	0·0101	9·38
150	0·0094	8·73
175	0·0088	8·18
200	0 0082	7·62

K here expresses in centigrade degrees the change of temperature that would be produced in a cubic foot of water by the quantity of heat that flows across a plate of iron 1 foot square and 1 foot thick

in one minute, the faces of the plate being maintained at a constant difference of temperature of one degree centigrade.[1]

The great merit of Forbes's method is that it seeks to determine the conductivity directly in terms of its definition instead of through a solution of Fourier's equation, which is founded on the hypothesis of constant conductivity, and on Newton's law of cooling. The experiments have been repeated by Professor Tait,[2] with Forbes's iron bar, and they were also extended to other metals with the object of testing in what manner the thermal conductivity varied with temperature, and to determine if the variations of thermal and electrical conductivity followed the same laws. For this purpose copper and lead were chosen, because they can be obtained pure and are not excessively expensive. Two specimens of copper were used—one (Crown) of the highest, and the other (C.) of the lowest electrical conductivity. An alloy (German silver) was also examined because the electrical conductivity of this substance varies little with temperature. Tait's experiments.

In such an investigation as this a considerable range of temperature is essential, and at high temperatures the experimental difficulties become enormously increased. The end of the bar was kept at a high uniform temperature, not by Forbes's method of melting solder which requires constant watching, but by a special gas-burner, furnished with a regulator devised by Dr. Crum Brown, which supplied the gas to the burner at a constant pressure. In practice the working of this arrangement was found to be almost perfect. Another difficulty arose in the displacement of the zero on the thermometers when exposed to high temperatures, and an uncertainty always attends the correction to be applied, on account of the portion of mercury which occupies the stem not being at the same temperature as that in the bulb. In the case of copper, and even with German silver, a further difficulty arose at high temperatures in the oxidation of the surface. The coating of oxide promotes radiation, and at different temperatures the surface becomes oxidised to different degrees, so that each set of experiments with the short bar can be strictly compared only with one part of the long bar. The heating of the short bar for the dynamical experiment was effected by placing it over a row of gas-jets while it was rotated round its axis, so as to become uniformly heated on all sides. Other methods, such as a hot air bath, were tried and abandoned, and it was found that in heating

[1] Fourier's units were minute, metre, and the interval 0° to 100° as unit of temperature.—*Théorie*, Arts. 68, 69.

[2] Tait, *Trans. Roy. Soc.*, Edinburgh, vol. xxviii. p. 717, 1879.

the bar it was more important to avoid oxidation than to secure absolute uniformity of temperature.

When the statical cooling curves were constructed, they were found to be not even approximately logarithmic, except for small intervals, and even then the axis was not usually asymptotic to the curve. In reckoning the area between the curve and the axis, a great difficulty arose in determining how much should be allowed for the portion (in theory, infinitely long but of finite area) which extended beyond the lowest temperature observed, and the error arising from this uncertainty becomes more important the lower the temperature. This difficulty did not arise, however, in the case of copper, for on account of the high conductivity of this substance the further end of the bar was kept in a large vessel of gutta-percha, through which cold water constantly circulated, so that its temperature was below that of the surrounding air, and the temperature gradient $d\theta/dx$ was nowhere very small. In all such experiments a small temperature gradient and slow flow of heat should be avoided, and for this reason the surface of a good conductor, such as a copper bar, should be smoked.

The results obtained by Professor Tait are contained in the following table. The units are the foot, minute, and centigrade degree, the unit of heat being the quantity required to raise the temperature of one cubic foot of the substance 1° C. The numbers consequently represent diffusivities, the diffusivity of a substance being defined as the conductivity divided by the thermal capacity per unit volume.

Temp.	Iron.	Copper (Crown).	Copper (C.)	German Silver	Lead.
°C.					
0	0·0149	0·076	0·054	0·0088	0·0152
50	0·0138	...	.	...	
100	0·0128	0·079	0·057	0·0090	0·0160
150	0·0121	...	. .	...	...
200	0·0114	0·082	0·060	0·0092	...
250	0·0109	...	...	...	...
300	0·0105	0·085	0·063	0·0094	...
350	0·0102	...	...	...	..

The last two numbers for iron are merely probable values deduced from the curve drawn to represent the others.[1]

[1] In Professor Tait's experiments on copper and other substances which are attacked by mercury, the thermometer holes were lined with thin iron shells in which mercury might be placed.

Lord Kelvin has suggested (Art. "Heat," *Ency. Brit.*) that the holes should be fitted

261. The Guard-Ring Method.—It has been already pointed out (Art. 259) that the absolute conductivity of a substance may be determined by what has been called the wall method—that is, by keeping the two faces of a plate of the substance at two known temperatures, and noting the quantity of heat which flows through a known area per second. The great difficulty of determining the exact temperatures of the faces of the plate, however, placed this method in disrepute, and the determinations of conductivity have been chiefly based upon the bar method, either by the method of steady flow already described, or by the variable or periodic process introduced by Ångström (Art. 264).

If, however, a very thick plate of the material be employed, the temperature may be taken at various points of its interior, and the uncertainty of the surface temperature may be avoided. An outline of an experiment conducted on this principle is roughly represented

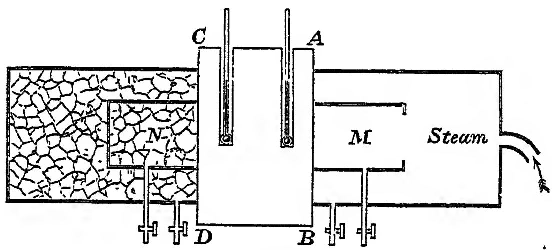

Fig. 145.

in Fig. 145. The plate under examination is ABCD. One face, AB, forms the end of a chamber filled with steam, and the other face, CD, forms the end of another chamber filled with ice. When the steady flow of heat is established, the lines of flow of the heat will be straight lines, perpendicular to the faces AB and CD, or, at any rate, this will be the case around the centre of the plate. Hence, if a known area of the central portion be isolated, and if the temperatures at any two points within the plate be determined by inserting thermometers (or couples), as shown in the figure, and if the quantity of heat which flows through this isolated portion be also determined, the conductivity of the plate will be known. To isolate the central portion a cylindrical chamber M may be fixed against the face AB. The steam, which condenses in M, can be drained off and weighed, and this will afford

with stems, and used as the bulbs of air thermometers. They might thus register their own temperature, but the method would probably be very difficult and uncertain in practice. In all cases some thermoelectric method would probably prove superior.

a measure of the quantity of heat which flows through the isolated section. Another measure of the same quantity may be obtained by fixing a similar cylinder N against the face CD, which, if filled with ice, will afford a measure of the flow by the quantity of ice melted per second. This may be roughly measured by allowing the water to drain off from N as the ice melts, and weighing it, but a much more accurate plan will be to make N the bulb of a Bunsen's ice calorimeter, and thus measure the quantity of ice melted by the diminution of volume.

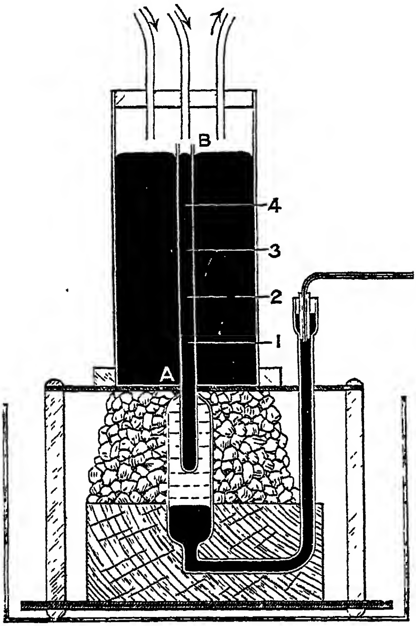

Fig. 146.

This method has been lately applied by M. Berget[1] with considerable success to mercury and some other metals. The apparatus adopted in the case of mercury is shown in Fig. 146. A cylindrical column of mercury AB, contained in a glass tube, was surrounded by another column of mercury, as shown in figure, which acted as a guard-ring, and prevented loss of heat by lateral radiation, so that the central column could be regarded as part of an infinite wall heated at its two faces to two constant temperatures, and if the conductivity does not vary with the temperature the distribution of temperature along the column will be linear. The essential part of the apparatus was a Bunsen's ice calorimeter, into which the column AB protruded. The mercury guard-ring rested on a sheet-iron plate, which in turn rested on the ice surrounding the bulb of the calorimeter. The mercury was heated at the top by steam, introduced by tubes, as shown in the figure. Through four apertures pierced in the side of the vessel which contained the mercury, thermoelectric junctions 1, 2, 3, 4 were inserted. These were simply four threads of iron wire, so that each pair of them, with the column of mercury between their ends, formed a thermopile which measured the difference of temperature between the ends of the pair.

Berget's experiments.

The greatest care was taken in reading the temperatures indicated

[1] Alphonse Berget, *Journal de Physique*, tom. vii. p. 503, 1888.

by these couples, and the results proved that the distribution of temperature along the column was linear. The mean value of K for mercury was found in this manner to be 0·02015 C. G. S. units. In all cases it was found that the times necessary for the establishment of the steady flow were proportional to the squares of the lengths of the column, which is a consequence of Fourier's theory.

The same method was also applied to metals, and the conductivity of copper was found to be 1·04050, of iron 0·1587, and of brass 0·2625.

262. **Thermal and Electric Conductivities—Variation of Thermal Conductivity with Temperature.**—It was first remarked by Forbes that the order of the thermal and electric conductivities of metals was the same—that is, that those metals which have the lowest electric resistance also conduct heat best. The analogy was pushed further by Wiedemann and Franz, who, from their experiments (p. 517), concluded that not only were the thermal and electric conductivities in the same order, but that they were sensibly in the same proportion, so that the ratio of the thermal to the electric conductivity was supposed to be the same for all metals. The truth of this conclusion has been the subject of many subsequent investigations, among which may be mentioned those of Ångström, Tait, Lenz, Weber, Kirchhoff, Hausemann, Lorenz, and Berget. When the electric conductivities are determined from wires, and the thermal from bars of the metal, it is not to be expected that any very reliable results should be obtained, for the drawing of the wires will alter the physical qualities of the substance, and it is well known that different specimens of the same metal differ considerably in conductivity, both for heat and electricity. Hence, although the conclusion of Wiedemann and Franz appeared to be confirmed by many subsequent investigators, it has been decisively contradicted by the experiments of Tait and Weber, and also by the recent investigations of M. Berget, so that although the order of conductivity is found to be the same, yet the further analogy has not been found to hold for all metals.

The change of thermal conductivity with temperature was also noticed by Forbes. The foregoing table (p. 524) shows a considerable decrease of conductivity with increase of temperature, and, as a similar decrease takes place in the electric conductivity of metals, it was supposed by Forbes that in general the thermal conductivities of metals, like their electric, diminished with rise of temperature. This generalisation was, however, proved to be erroneous by the subsequent investigations of Professor Tait,[1] who, although he also found a

[1] Tait, P. G., *Trans. Roy. Soc.*, Edinburgh, March 1878.

diminution in the conductivity of iron with rise of temperature, points out that the large variation obtained by Forbes partly arises from the fact that the variation of specific heat with temperature was neglected. In the great majority of investigations on the conduction of heat, it has been assumed that changes of specific heat with temperature do not require to be taken into account. Recent investigations, however, have shown that the specific heat of iron increases by as much as 1 per cent for every 7° C. rise of temperature, and when this is allowed for, the variation of conductivity obtained by Forbes becomes reduced to about $\frac{1}{5}$ of the original amount, a variation which, in such an exceedingly difficult investigation, might possibly be within the limits of experimental error.

The other metals examined by Professor Tait, on the contrary, showed an increase of conductivity with rise of temperature, and the analogy sought for by Forbes between thermal and electric conductivities was proved not to exist.

263. Flow of Heat in a Bar before the Steady State is acquired.—In the case of a bar heated at one end before the permanent state of steady flow is reached, a preliminary stage is passed through, in which the temperature of each element of the bar gradually rises. During this stage the difference between the quantities of heat which flow in at one face and out at the other face of a short length δx of the bar, is not all radiated from the surface of the element; but if the mean temperature of the element rises by an amount $d\theta$ in a time dt a quantity of heat

$$\mathrm{A}c\frac{d\theta}{dt}\delta x$$

is spent per second in raising the temperature of the bar, where c is the thermal capacity per unit volume—that is, the specific heat multiplied by the density of the substance. The equation of propagation therefore becomes

$$\mathrm{AK}\frac{d^2\theta}{dx^2} = \mathrm{E}p\theta + \mathrm{A}c\frac{d\theta}{dt}.$$

If the bar be surrounded by a guard-ring, or be coated with a non-conducting material, we may write $\mathrm{E}=0$, and the equation becomes

$$\frac{\mathrm{K}}{c}\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt},$$

or

$$k\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt},$$

where k is written for K/c, and has been termed the *diffusivity* of the material by Lord Kelvin. The same quantity has also been named

the *thermometric conductivity* of the substance by Clerk Maxwell, since it measures the change of temperature which would be produced in a unit volume of the substance by the quantity of heat which flows in unit time through unit area of a layer of unit thickness having unit difference of temperature between its faces.

It is this quantity that chiefly determines the effect of the heat conducted across any part of a body in heating the substance on one side, or cooling it on the other, and when this effect is to be reckoned it is convenient to measure the thermal conductivity in terms of this special unit, rather than of the ordinary water gramme unit of heat.

It may be remarked that the diffusivity k is of the dimensions l^2/t, and is consequently to be reckoned in units of area per unit time. In the C. G. S. system it is therefore expressed in square centimetres per second.

COR.—In the case of an infinite wall heated uniformly over one face, or a bar heated at one end and furnished with a guard-ring, when

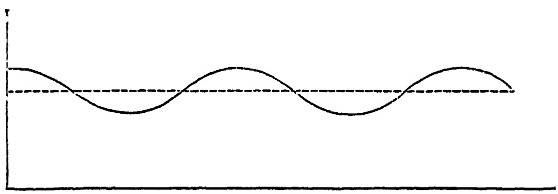

FIG 147.

the flow of heat becomes steady, the foregoing equation reduces to

$$\frac{d^2\theta}{dx^2}=0, \text{ or } \theta=ax+b,$$

that is, the temperature curve is a right line, if a and b are constants.

264. Periodic Flow of Heat through a long Bar.—If a long bar be periodically heated and cooled at one end, a thermometer sunk in it at any point will exhibit corresponding variations of temperature. When the end of the bar is heated a temperature wave travels along it, and the indication of the thermometer gradually rises. In the same way, when the end of the bar is cooled, the temperature registered by the thermometer will gradually fall, so that if the temperature of the end of the bar be varied periodically, the temperature at every point of the bar will also vary in a corresponding periodic manner, and when the periodic variation of temperature has been maintained for a sufficient time, the oscillations of temperature at any point of the bar will attain a fixed character, so that the mean temperature at each point remains steady.

If the periodic variation of temperature be a simple harmonic variation, then the variations of temperature at any point of the bar may be represented by a curve such as that of Fig. 147, and this curve will be a sine curve, $\theta = a \sin (at + \beta)$, where θ is the temperature, measured from the mean, and t the time. If, however, we consider the fluctuations of temperature at the various points of the bar, we find that the amplitude of the temperature variations at any point will diminish as the distance from the hot end increases, and at a certain distance along the bar the variations of temperature will be insensible, and the temperature of the bar will remain constantly equal to that of the surrounding medium (Fig. 148). The mean temperature at all points will not, however, be the same, but will diminish as we recede from the heated end, the curve of mean temperature being logarithmic, and similar to the temperature curves obtained by Despretz and Forbes. The fluctuations of temperature at each point will be periodic, but the variation of temperature near the heated end will be much greater than at some distance along the bar, the temperature waves gradually dying out as they proceed along the bar. These conclusions will appear clearly in the following analysis :—

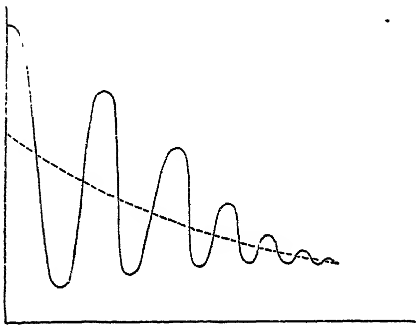

Fig. 148.

Let us take the case of a bar surrounded by a non-conducting jacket, and let a simple harmonic variation of temperature be applied to one end. In this case the temperature at any point is determined by the equation

$$k\frac{d^2\theta}{dx^2}=\frac{d\theta}{dt} \quad . \quad . \quad . \quad (1)$$

and a simple harmonic solution of this is

$$\theta=ae^{-\alpha x} \sin (\omega t+\beta x+\gamma) \quad . \quad . \quad . \quad (2)$$

if the constants ω, α, β be properly chosen. Differentiating (2) and substituting directly in (1) we find at once that in order that (1) may be satisfied by (2) we must have the relations

$$\alpha^2=\beta^2, \quad \text{and } 2\alpha\beta k= -\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now it is clear that if we confine our attention to a definite point of

the bar, so that x remains the same while t and θ vary, then θ will vary periodically, being the same when t increases by any multiple of $2\pi/\omega$. Hence, if the end of the bar be heated and cooled in a simple harmonic manner, the complete period of a heating and cooling being T, we have

$$\omega=\frac{2\pi}{T},$$

and consequently ω measures the rapidity of the alternations of temperature.

Let us now examine the time at which a thermometer placed in the bar at a distance x_1 from the origin will reach its highest or lowest temperature. This will happen when $\sin(\omega t+\beta x+\gamma)$ attains its greatest or least value—that is, when it is ± 1; or, in other words, the temperature will be a maximum at the point x_1 at the time t_1 given by the equation

$$\omega t_1+\beta x_1+\gamma=(2n+\tfrac{1}{2})\pi,$$

and the maximum temperature at a point x_2 will be reached at a time t_2, given by the equation

$$\omega t_2+\beta x_2+\gamma=(2n+\tfrac{1}{2})\pi,$$

the minima temperatures at the same points being reached when the values are $(2n-\frac{1}{2})\pi$. Hence by subtraction we obtain

$$\omega(t_1-t_2)+\beta(x_1-x_2)=0,$$

or

$$\frac{x_2-x_1}{t_1-t_2}=\frac{\omega}{\beta}.$$

Now, if the points x_1 and x_2 be so chosen that the maxima or minima of temperature occur at them simultaneously, we shall have t_2-t_1, equal to the periodic time T, and the difference of distance x_2-x_1 will be the length of the temperature wave λ, so that the last equation becomes

$$-\lambda=\frac{\omega}{\beta}T=\frac{2\pi}{\beta}.$$

Hence, in our original equation (2) for θ the quantities α and β are determined by the equation

$$\alpha=-\beta=\frac{2\pi}{\lambda}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

But the second equation of condition (3) gives

$$k=\frac{-\omega}{2\alpha\beta};$$

consequently, by substituting for a, β, and ω, we have the relation

$$k = \frac{\lambda^2}{4\pi T} \quad . \quad . \quad (5)$$

and when λ and T are known, we are furnished with the value of k.

This expression for k may also be written in the form

$$4\pi k = \lambda v,$$

where v is the velocity of temperature wave propagation (λ/T) along the bar, so that k is jointly proportional to the wave length and the velocity of propagation.

The equation (2) for θ may now be written in the form

$$\theta = e^{-\frac{2\pi x}{\lambda}} \sin 2\pi \left(\frac{t}{T} - \frac{x}{\lambda} + \frac{\gamma}{2\pi}\right),$$

Thus the amplitude of the temperature variation at any point x is $e^{-\frac{2\pi x}{\lambda}}$, so that the amplitudes go on decreasing as we recede from the heated end of the bar, and the mean temperature at any point diminishes in the same way, the ratio of the logarithms of the amplitudes at any two points being inversely as the distances from the end of the bar.

In order to determine the diffusivity by this method, it is consequently only necessary to measure the wave length λ corresponding to simple harmonic variation of temperature of known period T, and the conductivity may then be calculated in absolute measure when the thermal capacity of the substance per unit volume is determined.

If, however, the bar be not furnished with a guard-ring, but if radiation takes place from its surface, as in the experiments of Despretz and Forbes, the equation of propagation is

$$AK \frac{d^2\theta}{dx^2} = Ac \frac{d\theta}{dt} + Ep\theta,$$

or

$$k \frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \mu\theta,$$

where $\mu = Ep/Ac$.

A solution of this, which expresses simple harmonic variations of temperature in a long bar heated and cooled at one end, is again

$$\theta = ae^{-ax} \sin (\omega t + \beta x + \gamma);$$

but in this case the relations connecting the constants are found by substitution to be

$$a^2 - \beta^2 = \frac{\mu}{k}, \quad \text{and } 2a\beta = \frac{-\omega}{k},$$

from which it follows that

$$\alpha = \sqrt{\frac{1}{2k}\left\{(\omega^2+\mu^2)^{\frac{1}{2}}+\mu\right\}}$$

$$\beta = \sqrt{\frac{1}{2k}\left\{(\omega^2+\mu^2)^{\frac{1}{2}}-\mu\right\}}$$

as before $\omega = 2\pi/T$, while α is the rate of diminution of the Napierian logarithm of the temperature range, and β is the rate of retardation of phase reckoned in radians per unit length of the bar.

If the variation of temperature be not a simple harmonic variation it may be expressed as a sum of such variations if it be periodic, and the more general solution of the equation—

$$k\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \mu\theta,$$

which applies to any regularly periodic variation of temperature, will be

$$\theta = a_0 e^{-\alpha_0 x} + a_1 e^{-\alpha_1 x}\sin(\omega t + \beta_1 x + \gamma_1) + a_2 e^{-\alpha_2 x}\sin(2\omega t + \beta_2 x + \gamma_2) + \text{etc.},$$

if the constants be properly chosen. Differentiating and substituting this value of θ in the equation, we find that in order that it may be satisfied we must have

$$\alpha^2_0 = \frac{\mu}{k}, \quad k(\alpha^2_n - \beta^2_n) = \mu, \quad 2k\alpha_n\beta_n = -n\omega.$$

From which we derive

$$\alpha_n = \sqrt{\frac{1}{2k}\left\{(\mu^2+n^2\omega^2)^{\frac{1}{2}}+\mu\right\}}$$

$$\beta_n = \sqrt{\frac{1}{2k}\left\{(\mu^2+n^2\omega^2)^{\frac{1}{2}}-\mu\right\}}$$

where as before $\omega = 2\pi/T$.

265. Ångström's Experiments.—The first experimental determination of conductivities by the periodic method was made by the Swedish philosopher Ångström.[1] Long bars were employed, and the periodic heating and cooling was effected by enclosing a short portion of the middle of the bar in a vessel CD, as shown in Fig. 149, through which could be alternately passed a current of steam and a current of cold water.[2] When this heating and cooling had been continued for

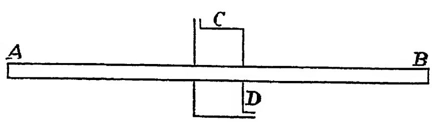

Fig. 149.

[1] Ångstrom, *Phil. Mag.*, vol. xxv. p. 130, 1863; and vol. xxvi. p. 161; *Pogg. Ann.*, B. cxiv. p. 513, 1861; and *Ann. de Chimie et de Physique*, 3e, tom. lxvii. p. 379.

[2] This was adopted with the copper bar, but the iron bar was cooled simply by radiation.

some time, the temperature at each point of the bar became steadily periodic, and the mean value of the temperature at any point became constant. Rigorously speaking, however, an infinite time is required to reach this stage. The bars were perforated at intervals of 50 mm. by cavities 2·25 mm. in diameter, which contained the bulbs of thermometers provided with arbitrary scales.

In making an experiment the heating was applied for twelve minutes and the cooling for the same time, so that the periodic time T was twenty-four minutes. The temperature at a given point of the bar was observed for each minute during one or more of these periods; and since at a given point the only variable in the general expression for θ is the time, the equation for θ may be written in the form

$$\theta = A_0 + A_1 \sin(\omega t + \delta_1) + A_2 \sin(2\omega t + \delta_2) + A_3 \sin(3\omega t + \delta_3) + \text{etc.},$$

in which, from the observations of θ, corresponding to various values of t, the constants A_0, A_1, etc., δ_1, δ_2, δ_3, etc., can be calculated. In practice the series may be limited to the first three or four terms, as the coefficients A_1, A_2, A_3, etc., decrease rapidly. Let us now suppose that similar observations are carried out at another point of the bar, and that the temperature at this point is given at the time t by the series

$$\theta' = A'_0 + A'_1 \sin(\omega t + \delta'_1) + A'_2 \sin(2\omega t + \delta'_2) + \text{etc.}$$

If the first series corresponds to a point x and the second to a point x', we have, using the notation of the foregoing article,

$$A_1 = a_1 e^{-\alpha_1 x}, \quad \text{and } A'_1 = a_1 e^{-\alpha_1 x'}$$

with similar expressions for the other coefficients, so that if the distance $x' - x$ between the two points be denoted by l, we have

$$\frac{A_1}{A'_1} = e^{\alpha_1 l}, \quad \text{while } \delta'_1 - \delta_1 = \beta_1 l.$$

therefore

$$\alpha_1 l = \log(A_1/A'_1),$$

and consequently

$$\alpha_1 \beta_1 l^2 = (\delta'_1 - \delta_1) \log(A_1/A'_1).$$

But we have already found that

$$-\alpha_1 \beta_1 = \frac{\omega}{2k} = \frac{\pi}{kT},$$

and hence

$$k = \frac{\pi l^2}{T(\delta_1 - \delta'_1) \log(A_1/A'_1)}.$$

In the same manner, if we had employed the terms involving A_n and A'_n, we should have had

$$A_n = a_n e^{-\alpha_n x}, \quad \text{and } A'_n = a_n e^{-\alpha_n x'}.$$

Therefore

$$\frac{A_n}{A'_n} = e^{\alpha_n l}, \quad \text{and } \delta'_n - \delta_n = \beta_n l,$$

consequently

$$\alpha_n \beta_n l^2 = (\delta'_n - \delta_n) \log (A_n / A'_n).$$

But

$$2k\alpha_n \beta_n = -n\omega,$$

therefore

$$k = \frac{n\pi l^2}{T(\delta_n - \delta'_n) \log (A_n / A'_n)}.$$

Thus each pair of terms leads to an independent determination of the quantity k, but the value obtained from the first pair is most reliable. The accuracy of the obtained value of k may also be controlled by altering the period of heating and cooling.[1]

Ångström's first experiments were made with square bars 570 mm. long and 23·75 mm. side, and the value found for the conductivity of copper and iron at the mean temperature of 50° C. were—

For copper . .	$K = 54{\cdot}62$
For iron .	$K = 9{\cdot}77$

the units employed being the centimetre, gramme, and minute.

A subsequent series of experiments[2] on bars 1178 mm. long and 35 mm. thick, furnished with thermometers at intervals of 200 mm., and in which the heating apparatus was so modified that different mean temperatures could be obtained, gave in the same units—

For copper . . .	$K = 58{\cdot}94\ (1 - 0{\cdot}0015190\theta)$
For iron	$K = 11{\cdot}927\ (1 - 0{\cdot}002140\theta)$

This method when applied with proper precautions is undoubtedly capable of furnishing good results. In practice, however, the use of ordinary mercury thermometers is not advisable in the determination of rapidly varying temperatures, as they are always tardy in their indications and liable to work by sudden starts. For the measure-

[1] The value of k may also be deduced, without using β, when α is known for two different periods. For the general expression for α is

$$2k\alpha^2 = (\mu^2 + n^2\omega^2)^{\frac{1}{2}} + \mu,$$

or

$$4k^2\alpha^4 - 4k\alpha^2\mu = n^2\omega^2.$$

Similarly for a different period ω' we have

$$4k^2\alpha'^4 - 4k\alpha'^2\mu = n^2\omega'^2.$$

Therefore, eliminating μ, we obtain

$$k = \frac{n}{2\alpha\alpha'} \sqrt{\frac{\omega^2\alpha'^2 - \omega'^2\alpha^2}{\alpha^2 - \alpha'^2}}.$$

[2] Ångstrom, *Phil. Mag.*, vol. xxvi. p. 161, 1863.

ment of temperatures in all such cases the employment of thermo-electric couples would be much superior.

266. Conductivity of the Earth's Crust—Underground Temperatures.—The method of determining conductivities by periodic heating and cooling may be applied directly to the estimation of the conductivity of the earth's crust at any place. For by day the surface of the earth is heated and by night it is cooled, so that a series of heat waves are propagated into the interior, and if the length of the wave and the periodic time are known we have the data required for the calculation of k. There is also a general aggregate heating of the surface during the summer with a corresponding cooling during the winter, so that in addition to the diurnal waves, which are lost at a depth of 3 or 4 feet, there is an annual wave which may be traced to a much greater depth, but at a depth of 50 feet or more the temperature at each point remains sensibly constant throughout the year.

If, however, the mean temperatures at different depths be compared, they are found to increase as we descend to the greatest depths yet penetrated. The amount of this increase varies much with the locality and the nature of the strata in which the observations are made, being largely affected by water-percolation and other circumstances, so that in some places it is as much as 1° F. for 30 or 40 feet, whereas in others an increase of 1° F. corresponds to a descent of 120 or 130 feet. Roughly speaking, however, the rate at which this increase takes place in this country is about 1° F. for every 60 feet of descent. This gradual increase of temperature as we descend proves that there must be a flow of heat from the interior through the surface, and the amount of heat which escapes from the earth per annum in this manner may be estimated when the conductivity of the crust is known. Having calculated the present rate of loss, we can calculate backwards what the temperature of the earth must have been in time past, and in this manner Lord Kelvin[1] has shown that it cannot be more than 200,000,000 years since the earth was a molten mass, on which a solid crust was just beginning to form.

If the crust at any place be supposed homogeneous, and if the eriodic variations of temperature be regarded as uniform, then the roblem of the propagation of heat-waves through it is the same as hat of an infinite wall periodically heated and cooled over one face, the same as that of a bar periodically heated at one end and coated ith a non-conducting material or a guard-ring. If, therefore, a umber of thermometers be buried with their bulbs at different depths low the surface, the inward progress of the annual wave may be

[1] Sir William Thomson, *Trans. Roy. Soc.*, Edin., vol. xxiii., 1862.

determined and the wave length estimated. In the case of a simple harmonic variation of temperature we have (p. 534)

$$k=\frac{\lambda^2}{4\pi T},$$

which, with the thermal capacity per unit volume of the material, determines the absolute conductivity K.

The diurnal waves become insensible at so small a depth that in most localities the inequalities of the soil and drainage prevent any satisfactory observations on their inward propagation being carried out. At depths exceeding 3 feet the daily variations become insensible, and the changes observed are due to daily averages (varying from day to day) which constitute the annual wave. If the annual variation were truly periodic, a complex harmonic function could be determined which would represent for all time the temperature at depths below 3 feet. But the annual variation is by no means perfectly periodic, since there are differences in the annual average temperatures and continual irregularities in the progress of the variation within each year. Sources of such disturbances are the unequal percolation of water and irregularities on the surface and within the crust.

If, however, the temperature be supposed periodic and be expressed as a complex harmonic function, and if the constants of the series be determined by observations on a thermometer buried at a certain depth, and if the constants of another series representing the varying temperature at another depth be determined in the same way by observations on another thermometer, then the comparison of each term of one series with the corresponding term of the other furnishes a determination of the conductivity, and all the values derived in this manner should agree perfectly if the data are accurate and if the assumed conditions are fulfilled—that is, if the isothermal surfaces are parallel planes, and if c and k are constant throughout the material.

These conditions, however, are not strictly fulfilled, and the first thing to be tested is how far the different determinations agree, and to learn accordingly how far the theory may be applied.[1]

[1] This method (Sir William Thomson, *Trans. Roy. Soc.*, Edin., vol. xxii. p. 405) differs from that followed by Forbes in substituting the consideration of the separate terms of a complex harmonic function for the examination of the whole variation unanalysed, which he conducted according to the plan laid down by Poisson. This plan consisted in using the formula for a simple harmonic variation, as approximately applicable to the actual variation. At great depths the amplitudes of the second and higher terms of the complex harmonic series become so much reduced that they do not sensibly influence the variation, which may consequently be expressed with sufficient accuracy by a single harmonic term of yearly period; but at the greatest depths, for which continuous observations had been made, Lord Kelvin

This difficult and laborious test has been applied by Lord Kelvin to the observations of Professor Forbes[1] on thermometers buried at different depths and in different soils near Edinburgh, and the analysis has proved that serious discrepancies from the theoretic formula existed, but these appeared to be attributable rather to irregularities in the form and constitution of the surface than to variations in the conductivity and specific heat of the material. Probably also thermometric errors considerably influenced the results, since there was necessarily some uncertainty in the corrections which must be applied to the stem in order to estimate the temperature of the bulb.

The following table contains the final results, the unit of length being one foot —

Substance	Diffusivity			Conductivity.		
	Per Ann.	Per 24 Hr.	Per Second.	Per Ann.	Per 24 Hr.	Per Second.
Trap rock of Calton Hill . . .	267·0	0·7310	·000008461	141·1	0·3863	·000004471
Sand of Experimental Garden .	295·0	0·8100	·000009374	88·9	0·2435	·000002818
Sandstone of Craigleith Quarry .	784·5	2·1478	·00002486	362·7	0·9929	·00001149

Much valuable information concerning the observations which have been made on the rate of increase of underground temperature downwards is contained in the Reports of the Committee of the British Association appointed for this purpose. A summary of the results contained in the first fifteen Reports (1868-81) has been drawn up by Professor J. D. Everett, the Secretary to the Committee, in which the general questions affecting such observations are discussed. Two kinds of thermometers have been used—slow-acting thermometers and maximum thermometers. A slow-acting thermometer consists of an ordinary thermometer having its bulb embedded in stearine or tallow, the whole instrument being hermetically sealed within a glass jacket. These were placed in holes a few feet deep bored in newly-opened rock, such as is presented in mine works or tunnels. The holes were carefully plugged and made air-tight to exclude the influence of the external air. After the lapse of a few days the thermometers were withdrawn and read, the slow action permitting this to be done

found that the second term had a very sensible influence, and the third and fourth terms were by no means without effect on the variations at 3 and 6 feet from the surface.

[1] Forbes, *Trans. Roy. Soc.*, Edin., vol. xvi., part ii., 1846.

without any appreciable change taking place in its indication during the operation. The maximum thermometers employed were of two types—the Phillips and the Inverted Negretti,—both being sealed in strong glass jackets to prevent the bulbs from being affected by pressure when lowered to a great depth in water.

The thermoelectric method of Becquerel was also tested by Dr. Everett, and from the result of some laboratory experiments it was concluded that the method could not be relied on to yield satisfactory results. The following table contains some of the results, the depth stated in each case being that of the deepest observation utilised:—

	Depth in Feet	Feet for 1° F
Bootle Waterworks (Liverpool) .	1392	130
Przibram Mines (Bohemia) . .	1900	126
St. Gothard Tunnel[1] .	5578	82
Mont Cenis Tunnel[1] . .	5280	79
East Manchester Coal-field	2790	77
Paris Artesian Wells	1312	56·7
London Artesian Wells (Kentish Town) .	1100	55
Yakoutsk, frozen ground (Siberia)	540	52
Sperenberg, boring in salt (Berlin) .	3492	51 5
St. Petersburg, well (Russia) . .	656	44
Carrickfergus, shaft of salt mine . .	770	43
,, ,, ,, . .	570	40
Slitt Mine, Weardale (Northumberland) .	660	34

Interesting observations have been recently made in a very deep bore (4500 feet) in Wheeling, West Virginia, by Mr. Hallock.[2] Beginning at a depth of 1591 feet (the upper portion of the bore was cased with iron tubes), the first 244 feet showed a gradient of 1° F. in 92 feet, the next 651 feet gave 1° in 84·5 feet, the next 746 feet gave 1° in 80·6, the next 643 feet gave 1° in 62·4, and the next 587 feet gave 1° in 58·1. The mean gradient for the whole 2871 feet (1591 to 4462) being 1° F. in 71·8 feet. At a depth of 4492 feet the mean temperature of some water in the bottom of the well was found to be 110·36° F.

[1] In the sixteenth Report it is mentioned that these numbers were derived from a conjectural correction for the convexity of the mountain surfaces. Dr. Stapff's calculations lead, however, to the conclusion that a much larger allowance must be made under this head. He deduces 1° F. in 85 feet as the average rate of increase from the surface above to the tunnel, and he calculates that at a depth below the tunnel, sufficient to make the isothermal surfaces sensibly plane, the increase is 1° F. in 57·8 feet.

[2] W. Hallock, *American Journal of Science and Art*, March 1892.

267. The General Equations of Conduction.—So far we have confined our attention chiefly to the propagation of heat along bars, or parallel to a single direction. The general case, however, in which

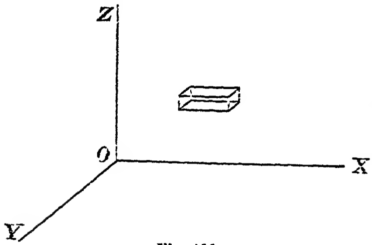

Fig. 150

the flow may take place in any manner may be treated by a similar method, and the general equations which determine it may be obtained without further difficulty. Thus if three mutually rectangular axes OX, OY, OZ (Fig. 150) be chosen as axes of reference, and if a small rectangular parallelopiped, having its edges parallel to the axes of reference, be considered, and if the lengths of the edges be δx, δy, δz, then confining our attention to the pair of faces perpendicular to the axis OX, it is clear that if the temperature at the central point of the parallelopiped be θ, the temperatures of the two faces under consideration will be

$$\theta + \tfrac{1}{2}\frac{d\theta}{dx}\delta x, \quad \text{and } \theta - \tfrac{1}{2}\frac{d\theta}{dx}\delta x,$$

for $d\theta/dx$ is the rate at which the temperature changes parallel to the axis OX—that is, the change of temperature per unit length in this direction, consequently

$$\tfrac{1}{2}\frac{d\theta}{dx}\delta x$$

is the difference of temperature between the centre of the parallelopiped and either end. It is of course understood that the element of volume is taken so small that the temperature over each face is sensibly uniform, and that the rate of change of temperature may be taken uniform along each edge.

The influx at the first face per second is consequently

$$-\mathrm{K}\delta y\delta z\frac{d}{dx}\left(\theta - \tfrac{1}{2}\frac{d\theta}{dx}\delta x\right),$$

while the efflux at the opposite face is

$$-\mathrm{K}\delta y\delta z\frac{d}{dx}\left(\theta + \tfrac{1}{2}\frac{d\theta}{dx}\delta x\right),$$

and hence it follows that the differences between the influxes and effluxes per unit time for the pairs of opposite faces are

$$\mathrm{K}\frac{d^2\theta}{dx^2}\delta x\delta y\delta z, \qquad \mathrm{K}\frac{d^2\theta}{dy^2}\delta x\delta y\delta z, \qquad \text{and } \mathrm{K}\frac{d^2\theta}{dz^2}\delta x\delta y\delta z.$$

The sum of these three quantities must consequently remain lodged in

the element, so that if the thermal capacity per unit volume be c, this sum must be equal to

$$c\frac{d\theta}{dt}\delta x\delta y\delta z,$$

for $d\theta/dt$ is the rate of change of temperature of the element—that is, the change of temperature per unit time. We have consequently the general equation—

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=c\frac{d\theta}{dt}.$$

If the temperature has become permanent at each point, so that a steady flow is established, we have $d\theta/dt=0$, and the equation of steady flow is therefore

$$\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}=0,$$

or, as it is generally written,

$$\nabla^2\theta=0$$

To determine θ as a function of x, y, z, t, it is necessary to know the manner in which the heat enters or leaves the body at the various points of its surface—that is, we want an accurate knowledge of the surface conditions. We might suppose, for example, that one part of the surface is kept in contact with a medium at uniform temperature θ_1, while the remainder of the surface is kept in contact with another medium at a different temperature θ_2. If θ_1 be higher than θ_2 then in the stationary state heat will enter the surface in contact with the first medium and escape by the surface in contact with the second, the quantity which enters being equal to that which escapes.

Thus if dn be an element of the normal to the element of surface dS, and h_1 and h_2 the coefficients of *exterior* conductivity for the first and second media, then we have the quantity of heat which passes through dS equal to

$$-K\frac{d\theta}{dn}dS=h_1(\theta_1-\theta)dS,$$

and for an element in contact with the second medium we have

$$-K\frac{d\theta}{dn}dS=h_2(\theta_2-\theta)dS.$$

These equations express the surface conditions necessary to the complete determination of the flow of heat and distribution of temperature.

268. Isothermal Surfaces, Lines, and Tubes of Flow.—In the general case the temperature at any point of a body will be a function

of the co-ordinates x, y, z, of the point and of the time t, so that the general expression for θ at any point will be of the form

$$\theta = f(x, y, z, t).$$

Hence, if we write

$$f(x, y, z, t) = a,$$

where a is a constant, we obtain the locus of all the points at which the temperature has the same value a at the time t. These points lie on a surface, determined by the function f, and named an *isothermal surface* because it is one of equal temperature. When the flow has become steady the temperature at any point remains steady, and therefore does not involve the time. In this case, then, the isothermal surfaces are fixed in shape and position, each separating those parts of the body which are hotter than a certain temperature from those which are colder. In the variable state, on the other hand, the shape and position of an isothermal surface corresponding to a definite temperature will in general vary with the time.

If a system of such surfaces be supposed drawn within the body, the temperature of each differing, by 1° suppose, from that which immediately precedes or follows it, the whole body will then be divided into a system of layers or shells such that the temperature of one face of each layer exceeds that of the other by 1°, and a flow of heat will proceed through the shell from the hotter face to the colder. The direction of the flow at each face will also be perpendicular to the surface, for since the temperature is constant all over each isothermal, it follows that there can be no flow along such a surface.

It follows then that the direction of the resultant flow at any point of a body is along the normal to the isothermal surface passing through that point, so that if a line be drawn cutting the whole system of surfaces orthogonally, the direction of the flow at every point of this line will be along the line. For this reason a line drawn so as to cut each of the system of surfaces at right angles is termed a *line of flow*.

The whole body may thus be imagined to be divided into a system of infinitely thin shells by a system of isothermal surfaces, and the infinite system of lines which can be drawn cutting these shells orthogonally are the lines of flow.

One property of these systems is that no two isothermal surfaces, or no two lines of flow, can intersect each other, for no point can possess two different temperatures at the same time, nor can the flow at any point be at once in two different directions.

If now we consider any closed curve drawn in the body, say a

curve traced on an isothermal surface, and if we imagine the lines of flow passing through each point of this curve to be drawn, then these lines will form a tube having the lines of flow lying in its surface. Such a tube is termed a *tube of flow*, and is such that there is no flux of heat across its walls, for it is bounded entirely by lines of flow, and no two such lines can intersect.

In the steady state it is clear that the total flow of heat across any isothermal surface is the same as that across any other, that these surfaces cut the tubes of flow orthogonally, and that the quantity of heat which crosses any section of such a tube per second is the same wherever the section be made. In fact, any heat that is once within a tube of flow must for ever remain within it, as there can be no flow across its walls.

Again, if we take two close isothermal surfaces, enclosing a thin shell, and if we consider two equal elements of area dS on different parts of the surface of this shell, then if $d\theta$ be the difference of temperature between the two faces, and dn the normal thickness of the shell at one of the chosen points, and dn' that at the other, the flows of heat per second through the two elements will be

$$\mathrm{Q} = -\mathrm{K}\frac{d\theta}{dn}d\mathrm{S}, \quad \text{and } \mathrm{Q}' = -\mathrm{K}\frac{d\theta}{dn'}d\mathrm{S}$$

respectively. Hence it follows that

$$\frac{\mathrm{Q}}{\mathrm{Q}'} = \frac{dn'}{dn};$$

or, in other words, the flow per unit area at any point of the shell is inversely as the thickness of the shell, so that where the shell is thinnest the flow is most rapid. In the same way it follows, from what has been stated concerning tubes of flow, that the flow per unit area through any cross-section of a tube of flow varies inversely as the area of the section, and combining these results, it follows that the tubes of flow are narrowest where the isothermal surfaces are closest, and *vice versâ*. All this, however, follows at once from our definitions (p. 509).

In the above equation we have supposed the conductivity of the material to be the same at each of its points; if this be not the case we have $\mathrm{Q}/\mathrm{Q}' = \mathrm{K}dn'/\mathrm{K}'dn$, so that the more general statement will be that the flow per unit area at any point of a shell bounded by two isothermal surfaces is directly proportional to the conductivity and inversely proportional to the thickness of the shell at this point.

Examples

1. A sphere is uniformly heated and then left to cool in a medium of uniform temperature.

In this case the isothermal surfaces are a system of concentric spheres, and the lines of flow are right lines passing through their common centre, while the tubes of flow are curves having a common vertex at the centre of the sphere. The lines and tubes of flow remain fixed while cooling proceeds, but the radius of the isothermal surface corresponding to a given temperature gradually contracts, the surface moving in towards the centre.

2. The centre of a sphere is kept at a constant temperature by a source of heat, while the surface is immersed in a medium of uniform lower temperature.

In Example 1 the temperature at each point gradually falls, and no state of steady flow is attained. In this case, however, there is a supply at the centre, and a state of steady flow from the centre towards the surface is established. Here the isothermal surfaces, as before, are spheres, but now they remain fixed in the body, and the total quantity of heat that flows across any surface per second is the same as that which flows across any other. Supposing the conductivity uniform, we have for this quantity

$$-\mathrm{K}\frac{d\theta}{dr}4\pi r^2 = \mathrm{Q},$$

and since Q is the same for all values of r, we have

$$-r^2\frac{d\theta}{dr} = a,$$

where a is a constant.

Hence

$$\theta = -\int\frac{a\,dr}{r^2} = \frac{a}{r} + b,$$

which gives the temperature at any distance r from the centre.

3. Two surfaces of a uniform spherical shell are kept at constant temperatures θ_1 and θ_2.

Let the radii of the two surfaces be r_1 and r_2. Then the temperature at any intermediate distance r is given by the equation of Example 2. The constants a and b are determined by the two surface conditions—

$$\theta_1 = \frac{a}{r_1} + b, \quad \text{and } \theta_2 = \frac{a}{r_2} + b.$$

Therefore

$$a = \frac{(\theta_1 - \theta_2)r_1 r_2}{r_2 - r_1}, \quad b = \frac{\theta_1 r_1 - \theta_2 r_2}{r_1 - r_2};$$

consequently

$$\theta = \frac{1}{r_1 - r_2}\left\{\theta_1 r_1 - \theta_2 r_2 - \frac{(\theta_1 - \theta_2)r_1 r_2}{r}\right\};$$

while the quantity of heat which flows across any isothermal surface per second is $4\pi\mathrm{K}a$, and the same quantity of heat would flow per second through an area $4\pi r^2$ of a wall of the same thickness as the shell and having its faces at the same difference of temperature $(\theta_1 - \theta_2)$, if r is the geometric mean of r_1 and r_2.

4. The internal and external surfaces of a long hollow circular cylinder are kept at fixed temperatures θ_1 and θ_2.

In this case the isothermal surfaces are coaxial cylinders, and the tubes of flow are wedges having their edges on the axis of the cylinder. The cross-section of any

one of these wedges by a plane parallel to its edge is a rectangle of constant length, and a breadth which varies directly as the distance from the axis. The area of the section consequently varies directly as its distance from the axis, and therefore the flow per unit area, in the steady state, varies inversely as the distance. Taking K constant, the equation of flow may therefore be written in the form, if the inner surface be hottest,

$$-\frac{d\theta}{dr}=\frac{a}{r},$$

where a is a constant, and hence

$$\theta=-a\log r+b.$$

The constants a and b are determined by means of the surface conditions

$$\theta_1=-a\log r_1+b,\quad \text{and } \theta_2=-a\log r_2+b$$

So that

$$a=\frac{\theta_1-\theta_2}{\log(r_2/r_1)},\quad \text{and } b=\frac{\theta_2\log r_1-\theta_1\log r_2}{\log(r_1/r_2)}.$$

The temperature at any distance r is consequently given by the equation—

$$\theta=\frac{\theta_1-\theta_2}{\log(r_1/r_2)}\log r+\frac{\theta_2\log r_1-\theta_1\log r_2}{\log(r_1/r_2)},$$

or

$$\theta=\frac{\theta_1\log(r/r_2)-\theta_2\log(r/r_1)}{\log(r_1/r_2)}.$$

The quantity of heat which flows per second across a length l of the cylinder will be

$$Q=-2\pi rlK\frac{d\theta}{dr}=2\pi aKl$$

$$=\frac{2\pi Kl(\theta_1-\theta_2)}{\log(r_2/r_1)}$$

If e be the thickness of the cylinder, we have $e=r_2-r_1$, and hence

$$\log\frac{r_2}{r_1}=\log\left(1+\frac{e}{r_1}\right)=\frac{e}{r_1}$$

if e be small. Hence for a thin cylindrical tube of radius r we have approximately

$$Q=2\pi Kl(\theta_1-\theta_2)\frac{r}{e}.$$

On the Conductivity of Crystals

269. Propagation of Heat in Æolotropic Substances.—In the previous investigations we have had under consideration the propagation of heat in isotropic substances—that is, in substances possessing the same physical characteristics not only in every part, but also in every direction around any point. When heat is supplied at any point of an isotropic body, the flow takes place equally in all directions around the point, and the isothermal surfaces are concentric spheres surrounding the heated point as centre. On the other hand, when any point of a heterogeneous substance is heated, the flow of heat in any

direction, and the shape of the isothermal surfaces, will depend upon the characteristics of the substance, or the manner in which its physical properties vary from point to point and from one direction to another. If the substance be homogeneous, however, but not isotropic, then, although its properties may be different in different directions around any point, yet the properties of the substance along any line are the same as those along any parallel line, so that when any two points are compared, the thermal conductivity and other properties of the substance along any line drawn from one point will be the same as along a parallel line drawn through the other. It follows, therefore, that when any point of a homogeneous substance is supplied with heat, the isothermal surfaces around it will be independent of the position of the point; or, in other words, those around one heated point will be similar, and similarly situated, to those around any other point. We shall see immediately that in general these surfaces are systems of similar ellipsoids, which become spheres, as a particular case, when the substance is isotropic.

The first experiments which established a difference of conductivity in different directions seem to be those of MM. de la Rive and de Candolle.[1] These philosophers proved that wood conducted heat along the fibre better than at right angles to it, and this conclusion has been confirmed by the subsequent investigations of Tyndall[2] and Knoblauch.[3] The conductivities in different directions were compared by the method adopted by Despretz (p. 515), blocks of wood being cut with pairs of opposite faces perpendicular to the fibre, parallel to the fibre, and perpendicular to the ligneous layers, and parallel to both the fibre and the ligneous layers, respectively. In all cases the conductivity was best along the fibre and worst in the direction perpendicular to the fibre and the ligneous layers—that is, along the radius from the centre to the bark of the tree. The following table, selected from Tyndall's results, will give an idea of the difference of conductivity in the ~~three~~ mutually perpendicular directions just mentioned. The numbers refer to the deflections of the galvanometer used in the experiments:—

[1] De la Rive and de Candolle, *Bibliothèque Universelle de Genève*, tom. xxxix.

[2] Tyndall, *Phil. Mag.*, 4th Series, vols. v. and vi.; and *Heat a Mode of Motion*.

[3] Knoblauch, *Pogg. Ann.*, vol. cv. p. 623.

Name of Wood.	Parallel to Fibre.	Perp. to Fibre and Parallel to Ligneous Layers.	Perp. to Fibre and to Ligneous Layers
Oak	34	11·0	9·5
Beech . .	33	10·8	8·8
Boxwood	31	12·0	9·9
Ash . .	27	11·5	9·5
Apple-tree ..	26	12·5	10·0
Scotch Fir	22	12·0	10·0

A similar difference of conductivity along and perpendicular to the planes of cleavage of laminated rocks which are not crystallised, has been detected by Jannettaz,[1] the conductivity being best parallel to the planes of cleavage and worst perpendicular to them. The same difference along and perpendicular to the planes of cleavage of bismuth has also been found by Svanberg and Matteucci. This difference in the case of laminated rocks shows that underground temperatures may be considerably modified by the inclination of the strata to the horizon.

270. Experiments of M. de Senarmont.—The first extended experimental investigation of the conductivity of crystals was that of M. de Senarmont.[2] The method adopted consisted in cutting a thin plate, with parallel faces, in any desired direction from the crystal. The surfaces of the plate were coated with a thin film of white wax, and heat was applied at one point, from which it was conducted in all directions through the plate. As the plate became warm the wax melted around the point, and the inequalities of conductivity in different directions were indicated by the shape of the bounding line of the melted wax.

In the case of isotropic substances, such as glass or cubic crystals, this curve was always a circle, and it was also a circle when the plate was cut in certain directions from crystals which did not belong to the cubic system, but in general with a plate cut in any other direction from a crystal the curve was elliptical, or at least an oval curve very approximately an ellipse. This line remained visible on the wax after the plate had cooled, and its eccentricity and the position of the axes of the curve could be determined. It would thus appear that the isothermal surfaces around a heated point of a crystal are in general a system of concentric ellipsoids.

[1] Édouard Jannettaz, *Journal de Physique*, tom. v. p. 150 ; and *Ann. de Chimie*, 4e, tom. xxix. p. 5, 1873.

[2] De Senarmont, *Ann. de Chimie et de Physique*, 3e, toms. xxi. xxii. xxiii., 1847-48.

It was also found that the axes of these ellipsoids, or the thermic axes, coincided with the crystallographic axes of symmetry, so that, for example, in crystals of the cubic system the propagation of heat took place as in uncrystallised media, and in crystals of the rhombohedral system the axis of the crystal was an axis of thermic symmetry, the isothermal surfaces being ellipsoids of revolution around it. It was found in this manner that quartz and calc-spar conduct heat best along the axis of symmetry, and equally in all directions perpendicular to this axis, while idiocrase and tourmaline conduct heat best at right angles to the axis.

One method of heating the crystalline plate is shown in Fig. 151. A small hole having been drilled through the plate AB, a copper or silver wire (being good conductors) was passed through it, and the lower portion MN was bent at right angles and heated by a lamp, the direct radiation of the lamp being carefully screened off. The wire soon becomes heated, and being a good conductor, the heat is carried

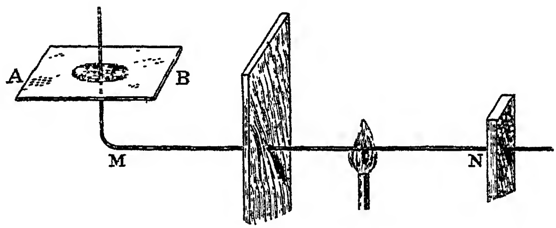

Fig. 151

to the plate, the wax melts around the hole, and an isothermal line corresponding to the melting-point of the wax is left imprinted on it.

In M. de Senarmont's experiments it was not a simple wire that was used, but a fine silver tube, so that when it became heated an ascending current of hot air flowed through it, and heat was carried to the plate both by the conduction of the metal and by the convection of the heated air. Two other methods of heating the plate were also employed. In one the rays of the sun were concentrated by a lens of short focus to a point on the surface of the plate, and in the other a wire was passed through the hole and heated by an electric current. The former method possesses an advantage in that the drilling of a hole is avoided, and no discontinuity is introduced into the plate, and in the latter method caution is necessary in heating the wire, for if the temperature be raised too suddenly the plate may be fractured.

When the plate is fairly thick, and heated by a wire passing

through a hole at right angles to its faces, the curves on its two faces are in general not true ellipses, but egg-shaped ovals, such as are shown in Fig. 152, having their more obtuse ends turned in opposite directions on the two faces. This arises from the fact that the plate is not heated at a single point, but along a line, and when the source of heat is a line, the curves on the two faces will be similar ellipses only when the line is in the direction of the diameter of the thermic ellipsoid, which is conjugate to the direction of the faces of the plate. This point will be brought out in the theoretical investigation which follows.

More recent experiments by Von Lang[1] and Jannettaz have extended to a great number of crystals the results obtained by De Senarmont, but they have brought to light no new or more general relations.

A determination of the absolute conductivities of crystals in different directions has been recently made by Mr. C. H. Lees,[2]

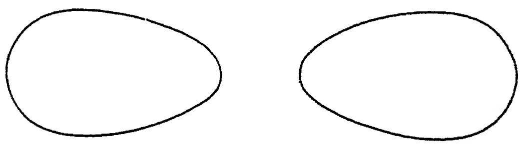

Fig. 152

according to a plan suggested by Professor O. J. Lodge.[3] This method consists in placing a slice of the crystal between the ends of two bars of metal placed end to end with their lengths in the same straight line. The crystalline lamina thus forms part of a compound bar which may be treated experimentally, either by the method of Forbes or by that of Ångström.

In order to secure good contact between the bars and the crystal, a metal (brass) was used which would amalgamate, and the contact given by the amalgamated ends was found to be extremely good. The temperature curve along the bars was determined by means of thermoelectric couples of iron and German silver soldered into the bars. The compound bar was packed in sawdust, and one end was heated by steam, while the other was immersed in cold water. When the temperature curve was plotted, the value[4] of $d\theta/dx$ could be

[1] Victor Von Lang, *Pogg. Ann.*, vol. cxxxv. p. 29, 1868.

[2] Charles H. Lees, *Memoirs and Proc. of the Manchester Phil. and Lit. Soc.*, vol. iv p. 17, 1890-91; *Phil. Trans.*, 1892.

[3] O. J. Lodge, *Phil. Mag.* (5), vol. v. p. 110, 1878.

[4] A correction for the thin layer of mercury between the metal and the crystal was determined by a special experiment.

determined for each face of the crystalline plate; and when the absolute conductivity of the brass bars is known, that of the crystal can be deduced. The absolute conductivity of the brass was determined by Forbes's method.

271. Theory of Conduction in Crystals.—The theory of thermal conduction in crystalline media was attacked as early as 1828 by Duhamel,[1] who from the hypothesis of molecular radiation deduced the general expressions for the flow of heat, and subsequently obtained a number of general consequences which applied directly to the experiments of M. de Senarmont. In 1851 the theory was presented by Stokes[2] in a form independent of any hypothesis of molecular radiation, the only assumption made being the general one that the quantity of heat is conserved, and, by means of an auxiliary solid, problems relating to crystalline conduction were reduced to corresponding problems concerning isotropic bodies.

Thus if we consider the flow of heat across an elementary plane area, drawn in a given direction, through any point P of the body, then if f be the flux of heat per unit area, per second, across this plane, the flow across the element dS in the time dt will be $f.d\mathrm{S}.dt$, and the value of f will depend on the direction in which the plane is drawn, and also on the time and the position of the point. For the present we shall consider the time and position given, so that f will depend only on the direction of the plane.

Let three rectangular planes of reference be chosen, and let f_x, f_y, f_z be the fluxes across them. Then if the elementary plane dS be supposed to approach indefinitely close to the origin, it will, with the planes of reference, enclose a small tetrahedron whose faces are dS, $\lambda d\mathrm{S}$, $\mu d\mathrm{S}$, $\nu d\mathrm{S}$ respectively, where λ, μ, ν are the direction cosines of the normal to dS. Now if the steady stage has been reached, as much heat flows into this tetrahedron as flows out; and even if this stage has not been attained, the difference between what flows in and what flows out will be vanishingly small compared with either, for it is proportional to the thermal capacity of the element and the rate of rise of temperature, but the former is proportional to the cube of the linear dimensions of the element of volume, whereas the fluxes across the faces vary as their areas or the squares of the linear dimensions. We may therefore equate the sum of the flows across any three faces to that across the fourth, so that we have

[1] Duhamel, *Journal de l'École Polytechnique*, toms. xxi. xxxii. See also Lamé, *Leçons sur la Théorie Analytique de la Chaleur*, Paris, 1861.

[2] G. G. Stokes, *Cambridge and Dublin Mathematical Journal*, vol. vi. p. 215, 1851.

the flow $f.dS$ per second across the base dS equal to the sum of the flows $f_x.\lambda dS$, $f_y.\mu dS$, $f_z.\nu dS$ across the other faces: or

$$f = \lambda f_x + \mu f_y + \nu f_z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation shows that if the fluxes of heat across the planes of reference be represented by three vectors, as in the case of forces or velocities, the flux across any other plane will be represented by the sum of the resolved parts of these vectors along the perpendicular to the plane. For some plane through P the flux of heat is greater than for any other, and the flux of heat across any other plane is this maximum flux multiplied by the angle between the planes.

Let θ be the temperature at P, and let us consider an elementary parallelopiped δx, δy, δz. The flow of heat per second through the face $\delta y\delta z$ is $f_x.\delta y\delta z$, and the flow through the opposite face is $(f_x + \frac{df_x}{dx}\delta x)\delta y\delta z$, and so on for the other pairs of faces, so that the gain of heat per second is

$$-\left(\frac{df_x}{dx} + \frac{df_y}{dy} + \frac{df_z}{dz}\right)\delta x\delta y\delta z.$$

But if the rate of change of temperature be $d\theta/dt$, and if the thermal capacity per unit volume be c, this must be equal to $c\delta x\delta y\delta z d\theta/dt$, and we have

$$\frac{df_x}{dx} + \frac{df_y}{dy} + \frac{df_z}{dz} = -c\frac{d\theta}{dt} \quad . \quad . \quad . \quad (2)$$

These formulæ are perfectly general, and apply whether the substance be homogeneous or not. We shall now suppose the material homogeneous, and that c is constant.

At this point a distinct assumption is made—namely, that the flow of heat at P depends not on the absolute temperature, but only on the variation of temperature in its vicinity. In fact, it is assumed that the flux across any plane is a linear function of the rates of change of temperature $d\theta/dx$, $d\theta/dy$, $d\theta/dz$, parallel to the axes, so that we may write

$$\left.\begin{aligned} -f_x &= \alpha_1\frac{d\theta}{dx} + \beta_1\frac{d\theta}{dy} + \gamma_1\frac{d\theta}{dz} \\ -f_y &= \alpha_2\frac{d\theta}{dx} + \beta_2\frac{d\theta}{dy} + \gamma_2\frac{d\theta}{dz} \\ -f_z &= \alpha_3\frac{d\theta}{dx} + \beta_3\frac{d\theta}{dy} + \gamma_3\frac{d\theta}{dz} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting these values of f_x, f_y, f_z in equation (2) we have

$$a\frac{d^2\theta}{dx^2} + b\frac{d^2\theta}{dy^2} + c\frac{d^2\theta}{dz^2} + 2f\frac{d^2\theta}{dydz} + 2g\frac{d^2\theta}{dzdx} + 2h\frac{d^2\theta}{dxdy} = c\frac{d\theta}{dt} \quad . \quad . \quad (4)$$

where $a = \alpha_1$, $2f = \gamma_2 + \beta_3$, etc.

Now there is a certain set of rectangular axes—namely, the axes of the quadric—

$$ax^2+by^2+cz^2+2fyz+2gzx+2hxy=1 \quad . \quad . \quad . \quad (5)$$

for which the equation (4) takes the form

$$A\frac{d^2\theta}{dx^2}+B\frac{d^2\theta}{dy^2}+C\frac{d^2\theta}{dz^2}=-c\frac{d\theta}{dt} \quad . \quad . \quad . \quad (6)$$

for if new axes of reference Ox', Oy', Oz' be chosen, making angles with the old axes Ox, Oy, Oz, whose direction cosines are l, m, n; l', m', n': l'', m'', n''; then

$$x'=lx+my+nz,$$

and

$$\frac{d}{dx'}=l\frac{d}{dx}+m\frac{d}{dy}+n\frac{d}{dz},$$

and since the symbols of differentiation combine with each other according to the same law as factors, it follows that the equation (4) will be transformed by a change of axes exactly as if the symbols of differentiation were replaced by co-ordinates x, y, z. When the principal axes of the surface (5), or any three conjugate diameters of it, are taken as the axes of reference, the equation (4) takes the form (6). These axes are termed the *thermic axes* of the crystal.

Taking the thermic axes as the axes of co-ordinates, the general expressions (3) for the flux of heat become simplified. The expressions (3) for f_x, f_y, f_z contain nine arbitrary constants; but when we substitute (2) and compare the result with (6) it follows at once that $\beta_1=-\alpha_2$, $\gamma_1=-\alpha_3$, $\gamma_2=-\beta_3$, so that the expressions may be written in the form

$$\left.\begin{aligned}-f_x&=\ \ A\frac{d\theta}{dx}-H\frac{d\theta}{dy}+G\frac{d\theta}{dz}\\ -f_y&=\ \ H\frac{d\theta}{dx}+B\frac{d\theta}{dy}-F\frac{d\theta}{dz}\\ -f_z&=-G\frac{d\theta}{dx}+F\frac{d\theta}{dy}+C\frac{d\theta}{dz}\end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

If the substance be symmetrical with respect to two rectangular planes, the coefficients F, G, H must vanish,[1] for the planes of symmetry must contain the thermic axes, and if these planes be taken as those of xz and yz, the expression for f_x must change sign with x, while f_y and f_z remain unaltered. Similarly f_y must change sign with y, while f_x and f_z remain unaltered, and referring to equation (7) this requires F, G, H to vanish, so that

$$f_x=-A\frac{d\theta}{dx},\quad f_y=-B\frac{d\theta}{dy},\quad f_z=-C\frac{d\theta}{dz}\ . \quad . \quad . \quad (8)$$

[1] Stokes, in the paper referred to, gives reasons for the supposition that F, G, H vanish in the general case.

The constants A, B, C are thus the conductivities of the substance in the directions of the thermic axes, and are termed the principal conductivities of the crystal.

Now, in the case of an isotropic substance the equation which determines the distribution of temperature is (p. 543)

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=c\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad (9)$$

and equation (6) which applies to a crystalline body will be transformed into an equation of the same form as (9) if the co-ordinates x, y, z be altered in the ratios $\sqrt{A/K}$, $\sqrt{B/K}$, and $\sqrt{C/K}$ respectively, or (9) will be transformed into (6) by altering the co-ordinates in the inverse ratio. And if we take $K^3 = ABC$, any volume of one will be strained by this transformation into an equal volume of the other. Hence the distribution of temperature in an isotropic solid, arising from any given conditions of heat supply at one or more points, being determined, the corresponding distribution, and the isothermal surfaces, in a crystal may be deduced by straining the co-ordinates in the manner just indicated. Derived solid.

Thus if heat be supplied at one point of an infinite isotropic solid according to any law, the isothermal surfaces will be spheres, and if the source be taken as the origin of co-ordinates, any one of these spheres will be given by the equation

$$x^2+y^2+z^2=r^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where r is the radius of the sphere. This surface becomes strained by the above transformation of co-ordinates into the ellipsoid

$$\frac{x^2}{A}+\frac{y^2}{B}+\frac{z^2}{C}=\frac{r^2}{K} \quad . \quad . \quad . \quad . \quad (11)$$

which is the corresponding isothermal surface in a crystal, the axes of reference being taken in the directions of the thermic axes of the crystal.

Hence in an infinite crystalline medium, if heat be introduced at a single point, the isothermal surfaces will be a system of concentric and similar ellipsoids, the axes of any one of which are directly proportional to the square roots of the three principal conductivities of the substance. Again, in the isotropic medium the flow of heat at any point takes place along the radius of the sphere, and varies inversely as the distance from the source, and the same result holds in the crystal. The flow across any plane touching the thermic ellipsoid is consequently in the direction conjugate to that plane.

Now, if an infinite isotropic plate be considered, and if heat be supplied at any point or any number of points along a normal to the plate, the isothermal surfaces will be surfaces of revolution round the normal, and the isothermal curves on the face of the plate will be circles. Hence, if a corresponding crystalline plate be heated at any point or at any number of points along a line (the line of sources) taken in the direction conjugate to the faces of the plate with respect to the thermic ellipsoid (11), any particular isothermal surface will be the surface generated by an ellipse moving with its plane parallel to the faces of the plate, its centre on the line of sources, and its principal axes parallel and proportional to those of the ellipse in which the thermic ellipsoid is cut by a plane parallel to the faces.

In the particular case in which the faces of the plate are cut parallel to the circular sections of the thermic ellipsoid, the isothermal curves on the faces will be circles, but the line joining the centres of the systems on the two faces will not be normal to the faces. In order, then, to procure ellipses on the faces of a plate in De Senarmont's experiment, it is necessary that the hole in the plate should be drilled in the direction conjugate to the faces with respect to the thermic ellipsoid.

In the same manner when a crystalline bar is heated at one end, the isothermal surfaces are not planes at right angles to the length of the bar, but are planes parallel to the diametral plane of the thermic ellipsoid, which is conjugate to the direction of the length of the bar.

Again, the flow of heat across any element of area in the crystal is equal to the flow across the corresponding element of the derived isotropic solid. For the flow across an element of area $dydz$ perpendicular to the axis of x in the crystal is $-\mathrm{A}\frac{d\theta}{dx}dydz$, and if $\mathrm{K}^3=\mathrm{ABC}$, this is equal to the flow across the corresponding area in the derived solid.

If we denote by Δ_x, Δ_y, Δ_z, the differences between the expressions (7) and (8), we have

$$\frac{d\Delta_x}{dx}+\frac{d\Delta_y}{dy}+\frac{d\Delta_z}{dz}=0,$$

which is analogous to the equation of continuity of an incompressible fluid.

SECTION II

ON THE CONDUCTIVITY OF FLUIDS

272. Conductivity of Liquids—Despretz's Method.—When the lower strata of a liquid are heated expansion occurs, and the consequent diminution of density causes the heated portions of the liquid to rise to the surface, while the colder parts sink to the bottom. In this manner convection currents are set up which transport the heat from one part of the liquid to another, and tend to bring about a uniformity of temperature throughout the mass. On the other hand, when the upper surface of the liquid is heated the warmer layers remain *in situ*, and the lower strata can become heated only by radiation and conduction proper, or by the process of diffusion or molecular convection—that is, by the individual molecules of the liquid becoming heated at the top and afterwards travelling into the lower strata, carrying their heat with them, and gradually parting with it to the colder molecules below by radiation or by contact, or by both processes simultaneously.

When heat is supplied at the upper surface of a liquid the flow of heat downwards is in general exceedingly slow, except in the case of mercury or other metals in the liquid state. In illustration of this we may cite the fact that the upper strata of water contained in a tube, at the bottom of which some ice is fixed, may be boiled without melting the ice below. Such a very feeble flow of heat might reasonably lead to the suspicion that in liquids the transport is mainly effected by molecular diffusion and convection rather than by that process of conduction which takes place in solids.

The earliest experiments of any note on the conductivity of liquids are those of Despretz,[1] the method adopted being analogous to the process applied to the determination of the conductivity of metal bars.

[1] Despretz, *Comptes Rendus*, 1838, p. 933; *Ann. de Chimie et de Physique*, vol. lxxi. p. 216, 1839. Earlier experiments on the passage of heat downwards through liquids were made by Murray (Nicholson's *Journal*, vol. i., 1802), and by Rumford (Nicholson's *Journal*, vol. xiv., 1806).

In operating on water a cylindrical wooden vessel B (Fig. 153) was employed, about 1 metre high and 20 cm. in diameter. At intervals of 5 cm. holes were drilled in the walls of the cylinder, and in these thermometers were inserted with their bulbs placed vertically over one another along the axis of the cylinder. The vessel was filled with water, and on the top of the liquid a copper box A was placed, which was kept filled with hot water renewed every five minutes. When this was continued for some time the upper thermometers were observed to show a gradual increase of temperature, and the wave of temperature proceeded slowly downwards, as long as thirty-six to forty hours being required before the stationary state was attained. This elevation of temperature could not be attributed to conduction of heat down through the sides of the feebly-conducting vessel, for Despretz, by means of other thermometers placed in the liquid, with their bulbs near the walls of the vessel, found that the temperature was higher along the axis than near the sides of the cylinder. Near the top the temperature did not vary much over a horizontal cross-section, but lower down this variation was considerable. It was thus proved that the propagation of heat takes place through the liquid either by molecular diffusion or by conduction proper or by both processes.

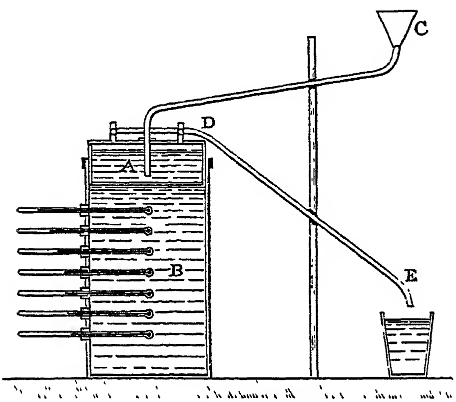

Fig. 153. Despretz's Apparatus.

Despretz specially observed the temperatures in the stationary condition, and he found that the distribution of temperature along the axis of the cylinder followed the same law as that in a long metal bar heated at one end and cooling by radiation in the open air. In this case we have already seen that the temperature curve is logarithmic and given by the formula

$$\theta = ae^{-\mu\lambda},$$

so that the relative conductivities of liquids may be determined in this manner like those of solids. Thus for liquids of conductivities K_1, K_2, K_3, etc., if lengths l_1, l_2, l_3, etc., correspond to equal differences of temperature, we have, as in the experiment of Ingen-Hausz,

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \text{etc.}$$

By a comparison of cylinders of the same material, Despretz found that μ varied inversely as the square root of the diameter of the cylinder, and this relation holds also for metals. The method, however, does not appear to be suited to give very accurate results, and the interest attaching to these experiments is chiefly historical.[1]

The same method was subsequently adopted by Paalzow,[2] in a slightly modified form, in an investigation of the relation, if any, between the electric and thermal conductivities of various liquids, and his observations prove that no relation exists between these quantities. For it appeared that water and sulphuric acid conduct heat almost equally, the former being somewhat the better.

Bottomley's experiments.

The conductivity of water, in absolute measure, has been obtained by Dr. J. T. Bottomley[3] by means of a modified form of Despretz's apparatus. The copper vessel employed by Despretz to contain the hot water, which acted as a source of heat, was dispensed with, and the heat was supplied by gently pouring hot water on the top of a wooden float of a diameter slightly less than that of the cylinder which contained the water to be experimented on, and on which the board floated. Two thermometers were placed with their stems horizontal and their bulbs on the axis of the cylinder at a short distance from each other. These thermometers gave the difference of temperature of the two faces of a horizontal stratum of the liquid of known thickness, and the quantity of heat which flowed through this stratum per second was calculated by observing the change of temperature of the whole mass of liquid below. This was indicated by a vertical thermometer, which had a long bulb extending downwards from the centre of the stratum in question to nearly the bottom of the vessel. Another thermometer was placed horizontally at the bottom of this upright thermometer in order to ascertain when the wave of temperature had travelled so far, and as soon as this occurred, which was not until the end of an hour, the experiment was stopped. The value found in this manner for the absolute conductivity of water in the C.G.S. system of units was

For water . . $K = 0{\cdot}002$.

The method, however, is by no means free from serious objections, especially in regard to the manner in which the quantity of heat which

[1] A valuable historical account of the conduction of heat in liquids has been given by Mr. C. Chree in the *Philosophical Magazine* for July 1887, vol. xxiv. p. 1.

[2] Paalzow, *Pogg. Ann.*, vol. cxxxiv. p. 618, 1868.

[3] J. T. Bottomley, *Phil. Trans. Roy. Soc.*, 1881, p. 537.

flows through the stratum is estimated, and the value 0·002 differs somewhat from that obtained by subsequent investigations.

273. More Recent Investigations.—The methods which have been since applied to the determination of the conductivities of liquids belong chiefly to two classes. One in which a layer of the liquid under examination is contained between two horizontal discs having their centres in the same vertical line, and the other in which the liquid is contained in the annular space between two coaxial cylinders.

Guthrie's experiments.

The first method, which may be termed the flat disc method, was adopted by Professor Guthrie[1] in 1869. His apparatus consisted of two equal hollow metal cones placed with their bases horizontal and at a small distance apart. The liquid under examination was introduced between the bases of the cones, where it was retained by capillarity. The lower cone contained air, and communicated with a tube containing a coloured liquid, so that it might be used as an air thermometer, the temperature of the air within the cone being determined by the height of the column of coloured liquid. The upper cone was kept heated by a current of hot water circulating through it. Apart from convection and conduction proper there are two ways in which heat may pass from the upper cone to the lower—namely, by radiation and diffusion. That the transference of heat by radiation is comparatively small may be inferred from the fact that several seconds elapsed after the application of the heat before any sensible movement of the coloured liquid was observed, besides, the insertion of a thin film of Swedish filtering-paper, which should greatly influence the radiation, scarcely affected the experiment. In order to determine how far diffusion took place, Guthrie painted the base of the upper cone with a soluble aniline dye, but on examination no trace of colour could be observed in the liquid near the lower cone, and he therefore concluded that diffusion had no sensible effect. These are the only points of importance which the experiments seem to establish. The other deductions are described by Mr. Chree as extremely fallacious, and the criticism does not appear to be unnecessarily severe, for the numerical results, although they are doubtless measures of something, are certainly not to be regarded as representing the conductivity of the liquid.

Weber's experiments.

Some very careful experiments have been made by Weber,[2] who also used the flat-plate method. These have been considered by Lorberg,[3] who has shown that the deductions of Weber in some

[1] Guthrie, *Phil. Mag.*, vol. xxxvii. p. 468, 1869.

[2] H. F. Weber, *Wied. Ann.*, vol. x. pp. 103, 304, 472; vol. xi. p. 347, 1880.

[3] H. Lorberg, *Wied. Ann.*, vol. xiv. pp. 291, 427; 1881.

respects require amendment. Weber's apparatus consisted of two copper plates, about 8 cm. in radius, placed one over the other, with their planes horizontal, the lower supporting the upper by means of three fragments of an ill-conducting material, so that the interval between them was 0·231 cm. The liquid was contained between these plates, as in Guthrie's experiments, and a small glass rim was employed in the case of the more mobile liquids. The temperature of the upper plate was determined by means of a thermoelectric couple, one junction being fused to the upper surface of the plate, while the other was immersed in ice. In making an experiment the apparatus was allowed to come to a stationary temperature, as indicated by the galvanometer, and the lower plate was then suddenly placed in contact with a block of ice; a screen of metal was then placed over the apparatus and the time was noted. After about two and a half minutes readings of the galvanometer were begun and continued at regular short intervals, so that the law of cooling of the upper plate was thus determined. This gave the rate of flow of heat through the liquid from the warmer to the colder plate, the assumptions made being that there was no sudden change of temperature in passing from the metal to the liquid, and that each plate was at the same temperature throughout.

The following table is extracted from Mr. Chree's paper. It contains the results obtained by Weber, and also those found by Lorberg for water, as well as the values obtained by Mr. Chree for glycerine and benzine by Lorberg's method. In each case Weber's result is placed first, and the units employed are the centimetre, gramme, and minute :—

Substance	Conductivity.	Substance.	Conductivity.
Water at 4°·1	0·0745	Alcohol	0·0292
,, corrected by Lorberg .	0·0831	Bisulphide of carbon .	0·0250
,, at 23·6	0·0857	Ether . . .	0·0243
,, corrected by Lorberg .	0·0911	Olive oil	0·0235
Copper sulphate solution . .	0·0710	Chloroform . . .	0·0220
Zinc sulphate solution . .	0·0711	Citron oil . . .	0·0210
,, ,, ,, . .	0·0698	Benzine	0·0200
,, ,, at 4°·5 . .	0·0691	,, corrected by Lorberg's method . . .	0·0235
Last solution at 23·44 . .	0·0776	Mercury at 4°·5	0·9094
Salt water at 4°·4	0·0692	,, corrected by Lorberg's method . . .	0·9250
,, ,, at 26·28 . . .	0·0809	,, at 17° . . .	0·9720
Glycerine at 6·25	0·0402		
,, corrected by Lorberg	0·0430		
,, at 25·2	0·0433		

Experiments by the coaxial cylinder or annular space method have

Winkelmann's experiments.

been made by Winkelmann and Beetz. The apparatus of Winkelmann[1] consisted essentially of two brass cylinders, one enclosing the other. The inner acted as the bulb of an air thermometer. For this purpose it was completely closed, save for a small hole at the centre of the upper end, in which a glass tube was fastened. This tube passed through a corresponding hole in the upper end of the outer cylinder, and could be fixed there, so that the two surfaces were parallel. It was then bent twice at right angles, so that its end dipped into a beaker of mercury. The height of the mercury in this tube varied with the temperature of the air within the cylinder, and could be thus used to register its temperature. The liquid under examination was enclosed in the annular space between the cylinders. In making an experiment the whole apparatus was plunged into ice-cold water, and the height of the mercury in the tube was noted subsequently at equal intervals of time while the apparatus cooled.

Denoting the temperature of the enclosed air before immersion by θ_0 and the velocity of cooling by v, Winkelmann estimated the temperature θ at a time t after immersion by the formula

$$vt = \log(\theta_0/\theta),$$

and he further assumed that the outer cylinder kept the temperature of the ice-cold water in which it was immersed, and that the inner cylinder and the liquid layer in contact with it were at the temperature of the enclosed air. He then estimated the temperature θ of the liquid at a distance x from the outer cylinder by the formula

$$\theta = \theta_0 e^{-vt}(ax + bx^2 + cx^3),$$

where a, b, c are constants determined by the assumed conditions at the bounding surfaces.

From observations with three different sizes of apparatus Winkelmann found that the conductivity supplied by the formula increased with the thickness of the liquid; but that very satisfactory results should not be obtained on the basis of so many assumptions is not surprising. Stirrers were employed to promote circulation in the bath and keep a constant supply of ice-cold water in contact with the outer cylinder, and the discrepancies were attributed by Winkelmann to the fact that these stirrers, although they might keep the curved surface of the cylinder at zero, did not renew the water sufficiently at the top and bottom, and to allow for this a correction was applied. According to Weber, however, who severely criticised this work, the discrepancies are to be attributed to convection currents.

[1] A. Winkelmann, *Pogg. Ann.*, vol. cliii. p. 481, 1874.

Winkelmann's results, expressed in centimetre, gramme, and minute units, are, for temperatures between 10° and 18° C.—

Water	0·092
Salt solution	0·1605
Alcohol	0·0904
Bisulphide of carbon . . .	0·1186
Glycerine	0·0449

The apparatus of Herr Beetz[1] consisted of a long cylindrical glass tube placed with its axis vertical, and enclosed within a coaxial glass tube of slightly larger dimensions, and fused to it near its mouth. The inner tube was filled with mercury up to a fixed level, and its mouth was closed by a cork which carried a thermometer with a long bulb which was completely immersed in the mercury. The liquid under examination was contained in the space between the two glass tubes; and the width of this space was small compared with the diameter of either tube, and the latter in turn was small compared with the length of either tube or with the length of the thermometer bulb, so that fairly good results should be expected from a treatment which regarded the liquid as enclosed between two infinitely long cylinders. Beetz's experiments

The main observations consisted of two series of experiments—one at a low and the other at a higher temperature. In the former the whole apparatus was immersed in an ice bath, and removed as soon as the thermometer indicated 1° C. It was then wiped dry, and when the thermometer indicated 2° C. the whole apparatus was immersed in a bath of water at 20° C. When the thermometer indicated 4° the time was taken, and the time of each successive rise of 2° was observed. In the second series the apparatus was immersed in a water bath at a temperature above 45°, and when the thermometer indicated 44° the apparatus was plunged into a bath at 20°, while the times of cooling each successive 2° were noted from the instant the thermometer registered 40°. For the velocity of heating or cooling Beetz employed the same formula as that used by Winkelmann, viz. $vt = \log(\theta_0/\theta)$, where θ_0 is the difference of temperature between the enclosed thermometer and the bath at the instant from which the time was reckoned, and θ the difference at the time t. The conductivity was determined by a formula which Weber pointed out must be incorrect. Fair results may, however, be obtained by multiplying Beetz's results by the specific heat of unit volume of the liquid. Errors must exist, however, in every case, for since glass is a bad conductor, the temperature will vary from one side to the other of each tube, however thin they be made.

[1] W. Beetz, *Wied. Ann.*, vol. vii. p. 435, 1879.

The question of convection currents was carefully considered by Beetz. He placed some lycopodium seed in the liquid and observed its movements through a microscope. In this manner he detected currents travelling up one glass surface and down the other. At the lower temperatures, however, he found that convection had no appreciable effect, for on thickening the water with meal he found scarcely any change in the conductivity, even when the water and meal had been boiled and allowed to cool to a thick paste. At higher temperatures, however, he found that convection played a decided part, and this goes far to justify Weber's objections against the experiments of Winkelmann. No change could be detected when colouring matter affecting radiation was introduced, and this agrees with Guthrie's observations.

The conductivities of several liquids have also been compared by means of a comparatively simple apparatus by Christiansen,[1] and Herr Grätz[2] has conducted a series of experiments on the same subject by the novel method of forcing a current of the liquid through a narrow pipe immersed in a bath containing water at a low temperature. The liquid was heated to a definite temperature before entering the pipe, and was forced through under a constant pressure, the quantity passing through per second being determined as well as the fall of temperature during its transit.

Lundquist's experiments.

The periodic method of Ångström has also been applied to liquids by Herr Lundquist.[3] The following table of his results has been given by Weber, who considers the method very accurate though tedious.

Substance.	Temperature.	Conductivity.	
		Lundquist.	Weber.
Water	40·8	0·0937	0·0953
Salt solution, density 1·178 .	43·9	0·0897	0·0901
Sulphate of zinc, density 1·382	45·2	0·0952	0·0872

The units employed are the centimetre, gramme, and minute. For the last liquid Lundquist took a specific heat 0·77, while the correct value, according to Weber, is 0·697, so that the corrected value of K would be 0·0862.

[1] C. Christiansen, *Wied. Ann.*, vol. xiv. p. 23, 1881.
[2] L. Grätz, *Wied. Ann.*, vol. xviii. p. 79; and vol. xxv. p. 337, 1885.
[3] Lundquist, *Upsala Universitets Arsskrift*, p. 1, 1869.

CONDUCTIVITY OF GASES

274. Andrews's Experiment—Conductivity of Hydrogen.—Difficult as the practical determination of the conductivity of liquids may be, the investigation becomes more complicated and perplexing in the case of gases, for here the phenomenon is masked by direct radiation, and it is almost impossible to determine how far the effects are due to convection and diffusion. For these reasons the determination of the thermal conductivity of gases is an investigation of extreme difficulty.

Many familiar facts, however, render it certain that heat is not conveyed with facility through air or other gases except by radiation. Thus the presence of interstices and cavities filled with air renders such materials as felt, wool, furs, etc., very bad conductors of heat. Such substances when compressed, so as to reduce the air cavities, conduct heat much better, and consequently become less warm when used as articles of clothing, but as to whether heat is propagated through the material more freely when the cavities are filled with air than when they are completely empty or filled with other gases must be tested by experiment.

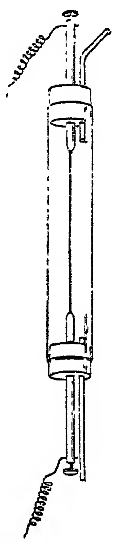

Fig. 154.

The experimental evidence on this subject points consistently to hydrogen as being a much better conductor of heat than any other gas, or at least that heat is much more freely propagated by this gas than by any other. A celebrated experiment on this subject is that described by Dr. Andrews,[1] and usually attributed to Grove. A thin platinum wire (Fig. 154), through which an electric current could be passed, was stretched within a glass tube. When the tube was filled with air, or any gas other than hydrogen, while the wire was raised to incandescence by the electric current, it was found that the brightness remained, though less vivid, when the tube was exhausted. On the other hand, when hydrogen was passed into the tube, the brightness of the wire was greatly diminished, or altogether annulled.

The experiment was varied by Grove,[2] who passed the same current through two similar wires stretched in different tubes, which could be filled with different gases. When one of the tubes contained hydrogen the wire in that tube was not luminous, although the wire in the other was vividly bright. This effect was found by Magnus to

[1] Andrews, *Proc. Roy. Irish Academy*, vol. i. p. 465, 1840.

[2] Grove, "Bakerian Lecture," *Phil. Trans.*, 1847; and *Phil. Mag.*, vol. xxvii. p. 445.

be very decided, even when the wires were stretched in very narrow tubes only 1 mm. in diameter, so that the layer of gas was very thin, and convection currents could scarcely occur, so that it appeared improbable that the whole cooling of the wire was caused by the mobility of the hydrogen molecules.[1]

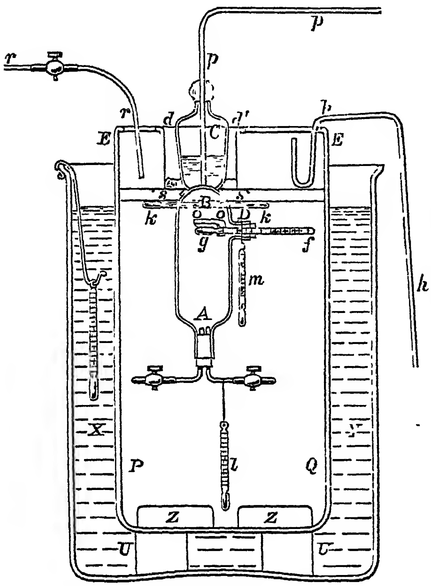

Fig. 155.

275. Experiments of Magnus.—The first notable investigation of the relative conductivities of gases was that published by Magnus[2] in 1860. The apparatus employed is shown in Fig. 155, and was similar to that already described in Art. 244. The investigation of the diathermancy of gases, in fact, developed out of the present inquiry concerning their conductivities. The gas under examination was contained in a very thin glass vessel AB, which was 160 mm. high and 56 mm. wide. The upper vessel C was

[1] Leslie had observed that a hot body cooled more rapidly in hydrogen than in air, and Dalton and Davy estimated the cooling powers of gases by observing the times taken by a thermometer to cool through the same number of degrees when placed in them. Their results, however, differed widely, and the question was attacked by Andrews by the novel method described in the text. Since the resistance of a wire increases with its temperature, it follows that if a current from a constant battery be passed through the wire this current will be greatest when the wire is immersed in those gases which keep it coolest. The wire was first heated in air, and then in another gas, and the current intensities compared in the two cases. The ratio of the current with wire in gas to that with wire in air was found as follows :—

Muriatic acid	0·958	Deutoxide of nitrogen	1·016
Sulphurous acid	0·967	Protoxide of nitrogen	1·019
Nitrogen	0·995	Oxygen	1·109
Carbonic oxide	1·003	Olefiant gas	1·171
Carbonic acid	1·010	Ammonia	1·118
Cyanogen	1·013	Hydrogen	1·382

The method was also extended to vapours, and it appeared that the cooling power of the vapours of ether and alcohol were considerably greater than that of air, and that of steam slightly greater.

[2] Magnus, *Pogg. Ann.*, vol. cxii. pp. 351, 497. Translated, *Phil. Mag.*, vol. xxii. p. 1, 1861.

fixed to AB by fusion, and contained water kept near the boiling point by a current of steam. This formed the source of heat, and in order to compare the indications of the thermometer when different gases were used, it was necessary that the vessel AB should be kept in an enclosure at constant temperature. For this purpose it was placed inside a cylinder PQ, which was surrounded by a bath of water XY, as shown in the figure. By this means the temperature of the inner enclosure was kept constantly at 15° C. A thermometer *fg* was fixed horizontally, and protected by a screen *oo* from the direct radiation of the source of heat above. In the earlier experiments a cork screen was used, but it was afterwards found that one of polished metal (silvered copper-foil) was much more efficient as a protection. This arises from the fact that the polished metal, although a better conductor than cork, is yet a much more feeble radiator and absorber. The following results give an idea of the difference in the indications of the thermometer when protected and unprotected in this manner in air at the pressure of one atmo.—

Cork Screen 2 mm. Thick.	Two Copper-foils 1 mm. Distant.	No Screen.
23° C.	21°·5	25°·5

When the steam is allowed to enter the vessel C the temperature indicated by the thermometer *fg* gradually rises, and in about half an hour becomes stationary—the time varying with the nature and pressure of the gas. This temperature depends on several circumstances, such as the conducting and radiating powers of the glass vessel AB, on the thickness and radiating power of the screen, and finally on the conductivity of the gas, and more or less on its diathermaneity. The results of the experiments are, however, comparatively simple. When the pressure of the gas was reduced to 15 mm. or less the stationary temperature of the thermometer was sensibly the same for all gases, and differed little from the temperature in vacuo. Denoting this latter by 100 (it[1] was 11°·7 C. with a cork screen 2 mm. thick, and 7°·8 with a metal screen), the corresponding numbers for the various gases at atmospheric pressure were as follows—

Substance.	Thermometer.	Substance	Thermometer.
Vacuum	100	Protoxide of nitrogen	75·2
Air	82·0	Marsh-gas	80·3
Oxygen	82·0	Olefiant gas	76·9
Hydrogen	111·1	Ammonia	69·2
Carbonic acid	70·0	Cyanogen	75·2
Carbonic oxide	81·2	Sulphurous acid	66·6

[1] The temperatures were counted from that of the surrounding medium, which was 15° C.

It appears from this table that the stationary temperature of the thermometer is higher in a vacuum than in any gas except hydrogen. The heat, therefore, travels through all these gases (except hydrogen) with less facility than through a vacuum. Further, the temperature of the thermometer rises as the gases are more rarefied, except in the case of hydrogen, for here the opposite effect was exhibited, the temperature falling as the hydrogen became more rare. This has been supposed to demonstrate the true conductivity of hydrogen, and to prove that the other gases possess no appreciable conducting power. It is, however, evident from the results that the other gases exercised quite as decided an effect as hydrogen, but in the opposite direction. The only certain inference we seem able to make is that the flow of heat to the thermometer, or the heat-carrying power of the space, is increased by hydrogen and diminished by the other gases, and there are no *a priori* grounds for the supposition that hydrogen possesses a conducting power similar to metals more than any other gas.

These experiments were repeated by Buff[1] with a somewhat similar apparatus. The mercury thermometer was, however, replaced by a thermoelectric couple of palladium and iron, and the walls of the enclosure were kept at a constant temperature by a cold water bath. The conclusions arrived at by Buff were that when perturbating causes are sufficiently guarded against no appreciable conduction effect is observable, and that the effect attributed to hydrogen arises from its great diathermancy rather than its conductivity. According to Buff, hydrogen is practically as transparent as a vacuum to radiant heat, whereas air absorbs as much as 50 or 60 per cent of the heat radiated by boiling water. This, however, is decidedly contradicted by many other experiments on the diathermancy of gases, which have been described already (Arts. 242-246). The indications of the thermometer in such experiments represent the resultant effect of several causes, and in no sense can they be regarded as representing the conductivity of the gas.

276. Absolute Conductivity of a Gas.—If a plane be imagined drawn through a mass of gas, then, according to the kinetic theory, the molecules are continually crossing from one side to the other of this plane, and by this process of interchange the properties of the gas tend to become equalised on both sides of the plane. Equalisation of temperature may thus be brought about by molecular diffusion, and the transport of heat through a gas by conduction is merely the transport of kinetic energy by molecular diffusion. The absolute conduc-

[1] H. Buff, *Pogg. Ann.*, vol. clviii. p. 177, 1876; and *Journal de Physique*, vol. v. p. 357, 1876.

tivity of a gas might then be defined as the quantity of heat, or kinetic energy, transported per second through a layer of the gas 1 cm. thick, 1 square cm. area, and having 1° C. difference of temperature between its faces, the transport being effected by molecular motions alone and not by the motion of large portions of the gas, such as takes place in convection currents.

To measure the conductivity of a gas consequently requires the study of their cooling under conditions in which the effects of convection currents are negligible.

This line of investigation has been followed by Kundt and Warburg[1] among others. When a thermometer is allowed to cool in a gas it loses heat by radiation, and also by conduction, but the effect due to the latter is completely masked by that arising from convection currents unless the pressure is small. When the pressure is diminished to a certain value the effects of convection currents become insensible, and the rate of cooling of the thermometer at any given temperature remains constant, until a stage of exhaustion is reached at which the mean free path of a molecule is not vanishingly small compared with the dimensions of the enclosure. This constancy of the rate of cooling is in accordance with the kinetic theory, from which it follows that the conductivity of a gas up to this limit is independent of the pressure.

Kundt and Warburg operated with three different enclosures, and found that with air the rate of cooling of the thermometer remained constant for pressures between 150 mm. and about 1 mm., and for hydrogen between 150 mm. and about 9 mm. Within these limits the action of convection currents was therefore insensible, and the observations lead to the conductivity of the gas when the cooling arising from direct radiation is determined. For this purpose the enclosure was exhausted as completely as possible after being thoroughly desiccated at a temperature of 200° C. In this state the rate of cooling was found to be independent of the shape of the enclosure, which showed that the effect of conduction by the residual gas was negligible. The radiation being thus known, the cooling produced by conduction was determined by difference.

By this means it was found that the conductivity of hydrogen was 7·1 times that of air, while the corresponding ratio for carbonic acid was 0·59. The former agrees with the theoretic deductions of Maxwell, but the latter is sensibly less than the value (0·7) obtained theoretically. The theoretic coefficient for carbonic acid is, however,

[1] Kundt and Warburg, *Pogg. Ann.*, vols. clv. and clvi.; and *Journal de Physique*, vol. v. p. 118, 1876.

unsatisfactory, as it depends on the ratio of the two specific heats, which varies with the temperature, and the theory does not take this into account.

The estimation of the absolute values of the conductivities required a knowledge of the thermal capacity of the thermometer, and, as this was not accurately determined, numerical results were not deduced. The value for air was, however, set down at 0·000048 in the C.G.S. system of units.

Stefan[1] observed the cooling of a thermometer furnished with a double envelope of copper and brass. The air between the two envelopes was thus heated by the interior and cooled by the exterior surface. The temperatures of these surfaces being known, and the rate of cooling being determined, the flow of heat through the layer of air can be deduced and the conductivity evaluated. The number found in this manner for air was 0·000056, which is 20,000 times less than that of copper. The dynamical theory led Maxwell to the number 0·000055. Stefan also found that, in accordance with theory, the conductivity was independent of the pressure, and that the conductivity of hydrogen was seven times greater than that of air. The effect of radiation is, however, neglected in the foregoing, and this renders the value of K somewhat too high.

The value deduced by Winkelmann[2] was 0·000052, and the variation with temperature was expressed by the formula—

$$K = K_0(1 + 0{\cdot}00277\theta).$$

According to theory, however, the conductivity should vary as the square root of the absolute temperature, and this result in itself is obvious, for under given circumstances the quantity of energy transported across any stratum of the gas will be proportional to the average velocity of translation, and, as we have already seen, this is proportional to the square root of the absolute temperature.

It is not, however, any part of our design to investigate the kinetic theory of gases fully in this place, so we shall at present consider only the following very simple case.

277. Simplest Case of Molecular Convection.—If the molecules of a gas be regarded as a system of equal and perfectly elastic spheres, and if the collisions between them be supposed to be all direct, then if their size and mutual attractions be neglected, it follows that after collision any pair of molecules have merely interchanged velocities,

[1] Stefan, *Sitzungsberichte der Wienerakademie*, vol. lxv. p. 42; and *Journal de Physique*, tom. ii. p. 147, 1873.

[2] A. Winkelmann, *Pogg. Ann.*, vol. clvi. p. 497, 1875; vol. clix. p. 177, 1876.

and if the time spent in collision is vanishingly small, the result is the same as if each molecule had pursued its course without interruption. These suppositions (which are made in the simple form of the dynamical theory) are consequently equivalent to assuming that the molecules move about independently, and are unimpeded in their courses by collisions or by any other mutual action.

Under such circumstances, if a gas is enclosed between two parallel planes A and A′ at a distance l from each other, and if the temperatures of these planes are θ and θ', then each molecule after impinging on A will recede from it and approach A′ with a velocity u determined by θ, while after impact with A′ it will rebound and approach A with a velocity u' determined by θ'. By this means, if we suppose θ greater than θ', there will be a convection of energy from A to A′ by the molecules, and the amount transferred in this manner per unit area per second may be easily calculated. For u being the component velocity perpendicular to the planes, the time of a journey from A to A′ will be l/u, while the time of return from A′ to A will be l/u', hence the whole time of the double journey (neglecting the time of rebound) will be

$$\frac{l}{u}+\frac{l}{u'},$$

and therefore the number of such journeys performed by each molecule per second will be

$$\frac{uu'}{l(u+u')}.$$

But if m be the mass of a molecule, the energy transferred by each molecule every journey will be $\frac{1}{2}m(u^2-u'^2)$, and consequently the energy transferred per second by each is

$$\frac{uu'}{l(u+u')}\tfrac{1}{2}m(u^2-u'^2)=\frac{muu'}{2l}(u-u').$$

Hence, if there are n molecules per unit volume, the number in operation in this case per unit area of the planes will be nl, and the quantity of energy transferred from A to A′ per unit area per second will be

$$\frac{muu'}{2l}(u-u')nl=\tfrac{1}{2}mnuu'(u-u').$$

Now if we represent $u-u'$ by a small quantity du, the energy transferred becomes

$$\tfrac{1}{2}mnu^2du,$$

and if we write $u^2=3\mathrm{R}\Theta$ in accordance with Art. 55, we have $2udu=3\mathrm{R}d\Theta$, and this expression becomes

$$\frac{3\sqrt{3}}{4}mn\mathrm{R}^{\frac{3}{2}}\sqrt{\Theta}d\Theta.$$

But since the planes are at a distance l apart, the expression for the conductivity, defined as in Art. 254, will be

$$Q=K\frac{d\Theta}{l},$$

therefore we obtain

$$K=\frac{3\sqrt{3}}{4}mnlR^{\frac{3}{2}}\sqrt{\Theta}.$$

When the size and mutual collisions of the molecules are taken into account, the investigation becomes much more complicated, but the foregoing should apply approximately to the case of two planes separated by a distance equal to the length of the mean free path. For if we consider the molecules rebounding from the plane A, then when each has on the average moved over the length of the mean free path it will collide with another molecule and return to A (the impacts being supposed direct); so that if a plane be drawn parallel to A, at a distance from it equal to the mean free path, the molecules in this layer may be regarded as remaining permanently in it, and vibrating between its faces, moving in one direction with the velocity u and returning with the velocity u'. In the same way the whole mass of gas between the planes A and A′ may be regarded as divided into a system of layers, each of a thickness equal to the mean free path, and the molecules in each layer may be regarded as remaining permanently in the layer, in a state of stationary vibration between its faces, instead of moving through the whole mass from A to A′.

Hence, if we take l in the above expression for K to be the mean free path of a molecule, then in the case of air at 0° C. and 76 cm. we have, in the C.G.S. system,

$$l=9\times 10^{-6},\quad R=2927,\quad \Theta=273,$$

and $mn=\rho=0{\cdot}001293/981$, which give

$$K=0{\cdot}00004.$$

CHAPTER VIII

THERMODYNAMICS

SECTION I

ON THE DYNAMICAL EQUIVALENT OF HEAT

278. Joule's Experiments.—The development of the dynamical theory of heat has been briefly sketched in Arts. 30-42 from the time of Rumford and Davy (who first placed it upon an experimental basis) up to the middle of the present century, when Joule completed his celebrated experiments on the dynamical equivalent, and forced the conclusions of Rumford and Davy upon the attention of the scientific

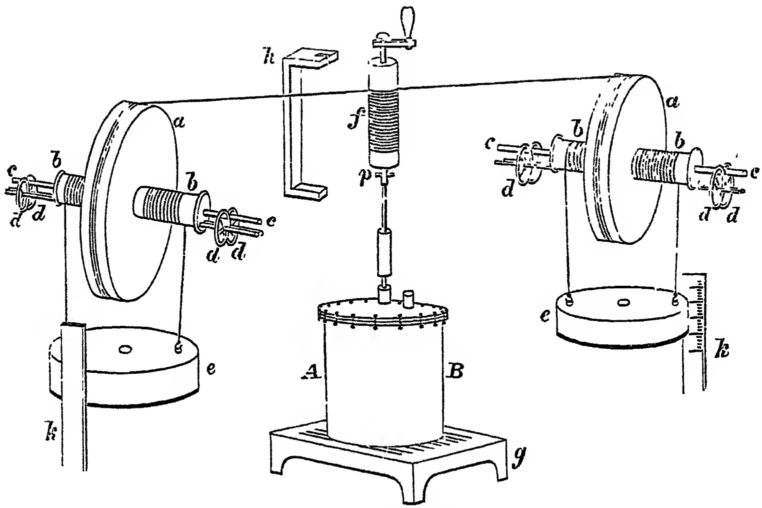

Fig. 156.—Joule's Apparatus.

world. These experiments have been already described in outline (Art. 35), but on account of the great importance of the dynamical equivalent as a physical constant, as well as the fundamental bearing of the principle of equivalence in the theory of heat, we shall now enter into a more detailed description of the investigations made in this department—investigations which would well merit a special attention if only as examples of the highest class of experimental research.

ascertained, the weights were wound up by placing the roller f in the stand h, and the roller was then pinned to the axis of the paddle. The height of the weights above the ground (about $5\frac{1}{4}$ feet) having been exactly determined by means of the graduated slips of wood kk, the roller was set at liberty, and allowed to revolve till the weights reached the floor. The roller was then unpinned and placed in the stand h, while the weights were wound up again, and the friction of the water was renewed. After this operation had been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the laboratory was determined by observations made at the commencement, middle, and termination of each experiment; and previous to, or immediately after, each experiment a test was made as to the effect of radiation and conduction of heat to or from the atmosphere in raising or depressing the temperature of the apparatus.

The following table is selected from Joule's [1] memoir, and will sufficiently indicate the mode of procedure. The leaden weights, together with the string attached, weighed 203066 grains and 203086 grains respectively. Their velocity on reaching the floor was 2·42 inches per second, and the time occupied by each experiment (twenty falls) was thirty-five minutes. The total fall of the weights during an experiment was therefore the sum of the heights passed over in twenty falls:—

[1] Joule, *Phil. Trans. Roy. Soc.*, 1850, pt. i.

[TABLE

I	II.	III.	IV	V	VI	VII
No. of Experiment and Cause of Change of Temperature.	Total Fall of Weights in Inches	Mean Temperature of the Air	Difference between Mean of V and VI. and III	Temperature of Apparatus. Initial.	Final.	Gain or Loss of Heat during Experiment.
		°	°	°	°	°
1. Friction	1256·96	57·698	−2·252	55·118	55·774	0·656 gain
1. Radiation	0	57·868	−2·040	55·774	55·882	0·108 gain
2. Friction	1255·16	58·085	−1·875	55·882	56·539	0·657 gain
2. Radiation	0	58·370	−1·789	56·539	56·624	0·085 gain
5. Friction	1251·81	60·940	−0·431	60·222	60·797	0·575 gain
5. Radiation	0	61·035	−0·237	60·797	60·799	0·002 gain
6. Radiation	0	59·675	+0·125	59·805	59·795	0·010 loss
6. Friction	1254·71	59·919	+0·157	59·795	60·357	0·562 gain
7. Radiation	0	59 888	−0 209	59·677	59·681	0·004 gain
7. Friction	1254·02	60·076	−0 111	59·681	60·249	0·568 gain
20. Radiation	0	60·567	−1·542	58·990	59·060	0·070 gain
20 Friction	1261·94	60·611	−1·239	59·060	59·685	0·625 gain
21. Friction	1264·07	58·654	−0·321	58·050	58·616	0·566 gain
21. Radiation	0	58 627	−0·018	58·616	58·603	0·013 loss
22. Friction	1262·97	58·631	+0·243	58·603	59·145	0·542 gain
22. Radiation	0	58·624	+0·505	59·145	59·114	0·031 loss
38. Radiation	0	55·826	−0·065	55·759	55·764	0·005 gain
38. Friction	1262 99	55·951	+0·093	55·764	56 325	0·561 gain
39. Radiation	0	56·101	+0·220	56·325	56·317	0·008 loss
39. Friction	1262·99	56·182	+0·409	56·317	56·865	0·548 gain
40. Friction	1262 99	56·108	+0·100	55·929	56·488	0·559 gain
40. Radiation	0	56·454	+0·036	56·488	56·492	0·004 gain
Mean Friction	1260·248	.	−0·305075	. .		0·575250 gain
Mean Radiation	0		−0·322950	...	. .	0·012975 gain

From the results of this series of experiments it was inferred that the heating or cooling effect of the atmosphere upon the apparatus was 0°·04654 for each degree of difference between the mean temperature of the apparatus and that of the air. The excess of temperature of the air over that of the apparatus was 0°·32295 in the mean of the radiation experiments, but only 0·305075 in the mean of the friction experiments. Hence 0°·000832 was added to the difference between 0°·57525 and 0°·012975, and the result, viz. 0°·563107, represented approximately the heating effect of the friction. To this quantity a small correction was applied on account of the mean of the temperatures of the apparatus at the beginning and end of each friction experiment having been taken for the true mean temperature, which was not strictly the case, owing to the somewhat less rapid increase of temperature towards the termination of the experiment when the water had become warmer. The mean temperature of the apparatus in the friction experiments was therefore estimated 0°·002184 higher, which diminished the heating effect of the atmosphere by 0°·00102, and this added

to 0°·563107 gave 0°·563209 as the correct mean increase of temperature due to the friction of water. This increase is a mixed quantity depending partly on the friction of the water, and partly on the friction of the vertical axis on its pivot and bearings. The latter, however, was only about $\frac{1}{80}$ of the former.

The total thermal capacity of the apparatus with the water contained was equivalent to that of 97480·2 grains of water, so that the total quantity of heat generated by friction was 0°·563209 in this weight of water, or 1° F. in 7·842299 lbs. of water. Now the weights amounted to 406152 grains, and from this a certain deduction must be made on account of the friction arising from the pulleys and the rigidity of the string. This was found by connecting the two pulleys with twine passing round a roller of equal diameter to that employed in the experiments. Under these circumstances the weight required to be added to one of the leaden weights in order to maintain them in equable motion was found to be 2975 grains.[1] The same result, in the opposite directions, was obtained by adding 3035 grains to the other leaden weight. Deducting 168 grains (the friction of the roller on its pivots) from 3005, the mean of the foregoing numbers, we have 2837 grains as the portion of the weight expended in friction of the pulleys and string. This subtracted from the leaden weights leaves 403315 grains as the weight available for the generation of heat in the apparatus.

A correction has still to be applied on account of the velocity possessed by the weights when they reached the floor. This velocity was 2·42 inches per second, and is equivalent to a fall through an altitude of 0·0076 inch. This multiplied by 20 (the number of falls in each experiment) gives 0·152 inch, which, when subtracted from the mean total fall, 1260·248, leaves 1260·096 inches as the corrected height. This fall of the above weights is equivalent to 6050·186 lbs. falling through a height of 1 foot, and to this is added $0{\cdot}8464 \times 20 = 16{\cdot}928$ foot-pounds as a correction for the elasticity of the strings, which comes into play after the weights have reached the ground.

The mean corrected result was therefore 6067·114 foot-pounds as the work spent in raising the temperature of 7·842299 lbs. of water 1° F., and this gives 773·64 as the dynamical equivalent of heat in the latitude of Manchester.

In Joule's second and third series of experiments the fluid employed was mercury, the apparatus being constructed of iron, and somewhat modified in other respects, to suit the purpose. In the fourth and fifth series the heat was developed, not by fluid friction,

[1] The number 2955 given in Joule's Memoir is probably a misprint.

but by means of a bevelled cast-iron ring rubbing against another bevelled iron ring in mercury. The following table contains the final results of these series of experiments, the fourth column giving the values when the weighings are made in a vacuum :—

No. of Series	Material employed	Equivalent in Air.	In Vacuum.	Mean.
1	Water	773·640	772·692	772·692
2	Mercury	773·762	772·814	774·083
3	,,	776·303	775·352	
4	Cast iron	776 997	776·045	774 987
5	,,	774·880	773 930	

Of these results, that derived from the friction of water was considered by Joule as the most reliable, both on account of the number of experiments performed, and the great thermal capacity of the apparatus. And since, even in the friction of fluids, it was impossible to entirely avoid vibration and the consequent expenditure of energy in sound, Joule thought it probable that the number 772·692 was slightly too large, and therefore adopted the round number 772. It must be remembered, however, that the unit of temperature employed here is the degree on the mercury thermometer[1] employed by Joule, and that the specific heat of water is taken as unity at the temperature of each experiment.

At the request of the British Association Joule[2] executed a new series of experiments, which he completed in 1878. In this investigation the arrangement of the apparatus and the principle of the method employed for measuring the work differed from that adopted in the earlier experiments. The calorimeter, h (Fig. 159), instead of sitting on a fixed stool, was suspended by a bearing on the vertical axis of the paddle, so as to be capable of rotating freely about it. With this arrangement, when the paddle was set in motion, the friction between the moving fluid and the walls of the calorimeter, as well as that which occurred at the bearing, produced a couple tending to turn the calorimeter round the vertical axis. The rotation of the calorimeter was prevented by an equal and opposite couple produced by the action of a fine silk cord, which passed round an accurately turned groove in the surface of the calorimeter. The ends of this cord were thrown over two light

[1] An error of 1 per cent may arise from want of comparison of the mercury thermometer with the air thermometer.

[2] Joule, *Phil. Trans. Roy. Soc.*, 1878, pt. ii.

wooden pulleys, *j*, *j*, and were attached to scale-pans, *k*, *k*, which contained weights sufficient to keep the calorimeter in equilibrium.[1]

The whole apparatus was contained in a massive wooden case, *aa*, which was divided into three compartments, and permanently boxed in on three sides. The fourth side or front was closed by shutters furnished with windows, which could be removed at pleasure. The paddle was kept in motion by means of doubling hand-wheels,

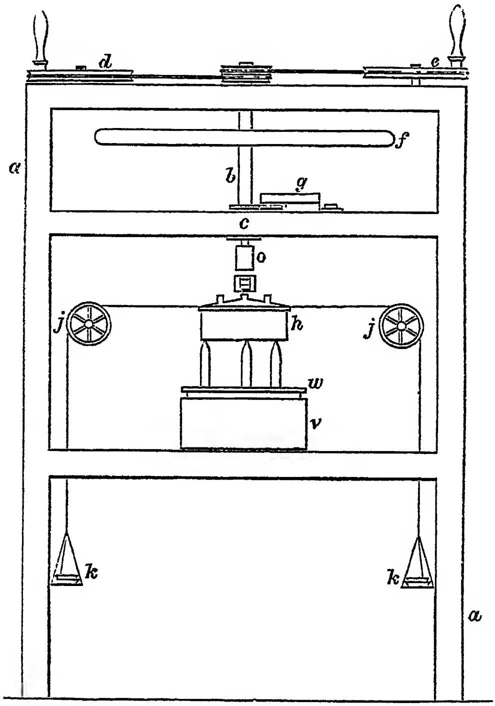

Fig. 159.—Joule's Later Apparatus.

de, and the vertical shaft, *b*, which carried a fly-wheel, *f* (weighing about 1 cwt.), was supported by a conical collar turned on it at *c*. The hydraulic supporter, *v*, *w*, was not employed in the initial stages of the investigation; but as irregularities were found to arise from time to time from the variations in the friction of the bearing which supported the calorimeter, the supporter, *v*, *w*, was designed, so that the pressure on the bearing and the metallic friction were almost reduced to zero. This supporter consisted of two concentric vessels,

[1] The principle of this method, which is a kind of friction balance, was designed by Hirn (*Théorie Mécanique de la Chaleur*, 3rd ed., p. 92), and was subsequently used by Rowland and others.

v and w. The lid of the inner vessel was surmounted by three uprights, and when water was poured into the space between the vessels the inner floated up, so that the uprights pressed against the bottom of the calorimeter, and the pressure on the bearing was thus relieved.

The calorimeter is shown in section in Fig. 160, and in plan in Fig. 161. There were four stationary vanes and two sets of rotating vanes, each of five arms, the upper set (dotted lines, Fig. 161) being fixed to the axis 9° behind the lower set, so that no two of the rotating vanes passed the fixed ones at the same moment, and as the momentary alteration of resistance at crossing took place forty times during each revolution, the resistance was practically uniform. The axle of the paddle worked easily in the collar m, and was screwed into the boxwood piece n. The boxwood piece o (Fig. 159) was intro-

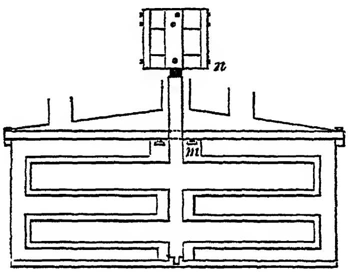

Fig. 160.

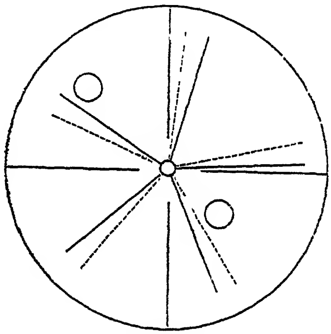

Fig. 161.

Section and Plan of the Calorimeter.

duced in order to prevent conduction of heat along the axis; but this precaution was found to be unnecessary.

In making an experiment the calorimeter was filled with a known weight of distilled water, and screwed on to the axis. Its temperature was noted, and the silk cord adjusted. The thermometer was then removed, and a caoutchouc stopper placed in the tubulure. The axle was then rapidly brought up to a speed sufficient to raise the weights about 1 foot from the floor, and they could be kept very steadily in this position during the whole time of an experiment (35 minutes). The wheel was then rapidly brought to rest, and the temperature of the calorimeter again noted.

The work spent is determined by knowing the number of revolutions and the moment of the couple required to keep the calorimeter in equilibrium. Thus, if w denotes the sum of the suspended weights, and r the radius of the calorimeter, the moment of the couple

tending to turn the vessel is wr, so that in turning through an angle θ the work done is $wr\theta$, or if n be the number of revolutions the work is

$$W = 2\pi nwr.$$

In calculating n, the number of revolutions of the axis when the weights were off the ground was added to half the number employed in the acts of starting and stopping the apparatus. The revolutions of the axis were registered by a counter at g (Fig. 159).

The results of five sets of experiments by this method are collected in the following table. In the first two sets the hydraulic supporter

Series.	Number of Experiments.	Proportion of Metallic to Total Friction.	Mean Rise of Temperature.	Temperature of the Calorimeter.	Equivalent.
1	17	$\frac{1}{7\cdot7}$	45·907	58·46	777·72
2	15	$\frac{1}{8\cdot3}$	48·803	54·76	774·57
3	21	$\frac{1}{106}$	44·777	59·98	773·136
4	6	$\frac{1}{43}$	14·355	58·14	766·97
5	7	$\frac{1}{108}$	67·620	63·14	773·99

was not employed, and the metallic friction at the bearing of the calorimeter was a considerable fraction of the whole.

The mean value deduced for J at the temperature of 60° F. was 773·369 foot-pounds at Manchester. This reduced to Greenwich and the sea-level becomes 773·492, or when the weighings are made in a vacuum the value of J at 60° F. is

772·55.

279. Rowland's Experiments.—In 1879 Professor Rowland,[1] feeling that Joule's work required to be extended in some directions and completed, undertook a careful and elaborate series of experiments on the value of the dynamical equivalent of heat. In Joule's work the experiments were made only at the ordinary temperatures of the atmosphere, and the mercury thermometers employed were not standardised by comparison with the air thermometer. Errors of 1 or 2 per cent may arise from this cause in calorimetric work, for even between 0°

[1] H. A. Rowland, *Proc. American Academy of Arts and Sciences*, New Series, vol. vii., 1879-80.

and 100° a difference of several tenths of a degree may exist between the mercury and the air thermometer.

The principal defect of Joule's plan of experiment, however, is the small rate of rise of temperature, and Professor Rowland, in designing his apparatus, aimed at procuring a large change of temperature in a

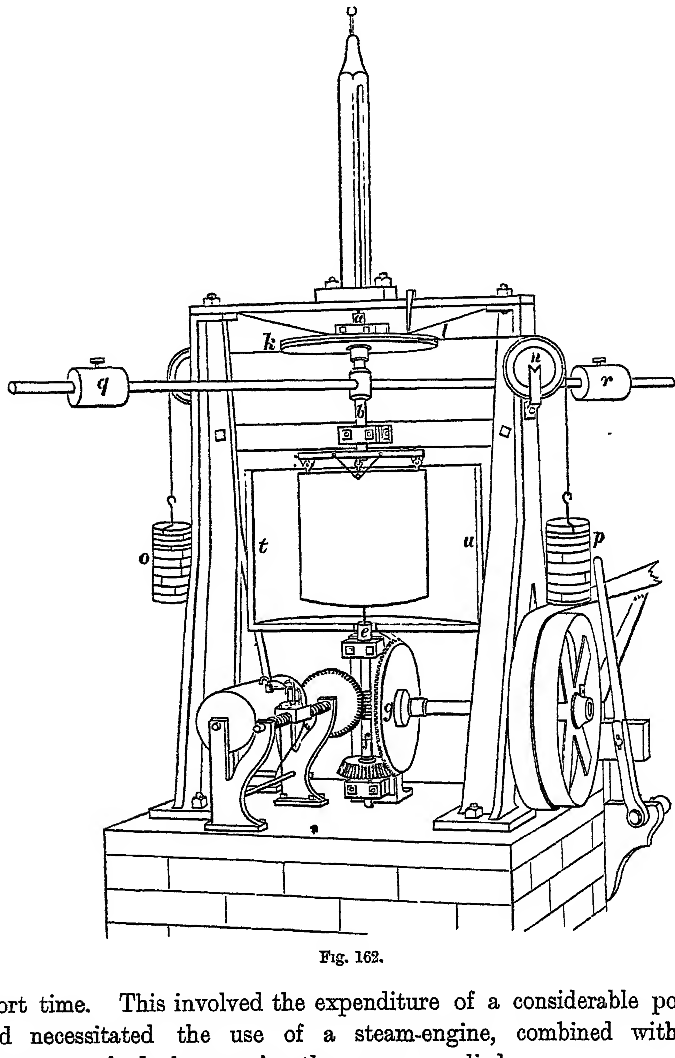

FIG. 162.

short time. This involved the expenditure of a considerable power, and necessitated the use of a steam-engine, combined with an accurate method of measuring the power supplied.

The apparatus finally adopted is shown in Fig. 162. In principle it resembles Hirn's friction balance and the apparatus employed by

Joule in his final experiments. The calorimeter was attached to a vertical shaft *ab*, and the whole was suspended by a torsion wire. The axis of the paddle left the calorimeter through the bottom and was attached to the shaft *ef*, which was kept in uniform motion by the wheel *g* driven by a steam-engine. To the axis *ab* an accurately turned wheel *kl* was attached, and the couple tending to turn the calorimeter was measured by weights *o* and *p*, attached to silk tapes passing around the circumference of this wheel, in combination with the torsion of the suspending wire. To this axis also a long arm was attached, having two sliding weights *q* and *r*, by means of which the moment of inertia could be varied or determined. The number of revolutions of the paddle was determined by means of a chronograph set in motion by a screw on the shaft *ef*. On this chronograph was recorded the transit of the mercury over the divisions of the thermometer. A water jacket *tu*, made in halves, was placed round the calorimeter, so that the radiation could be estimated, and a wooden box surrounded the whole and screened the calorimeter from the observer.

When the paddles were in motion, the couple tending to turn the calorimeter was balanced by the weights *o*, *p*, and the equilibrium was rendered stable by the torsion of the suspending wire. The amount of torsion was read off on a scale on the edge of the wheel *kl*, and this gave the correction to be applied to the weights *o*, *p*. One observer constantly read the circle *kl*, and another recorded the transits of the mercury over the scale divisions of the thermometer. In this manner a series of observations, extending over the space of half an hour to an hour, embraced a rise of temperature of from 15° to 25°, in which a record was made for perhaps each tenth of a degree, contained several hundred observations from any two of which the dynamical equivalent of heat could be obtained.

The correction for radiation is inversely proportional to the ratio of the rate at which the work is done to the rate at which the heat is lost, and this for equal ranges of temperature is only $\frac{1}{50}$ as great in these experiments as in Joule's, for Joule's rate of increase was only 0·°62 C. per hour, and in these experiments was about 35° C., and could be increased to over 45° C. per hour.

The calorimeter and paddle arrangement was more complicated than Joule's. The number of paddles was increased so that there should be no jerk in the motion, and that the resistance should be great. Their shape was also such as to cause the whole of the water to run in a constant stream past the thermometer, and to cause constant exchange between the water at the top and bottom. A section of the

calorimeter with paddle is shown in Fig. 163, and the paddle is shown separately in Fig. 164.

To a steel axis a stout copper cylinder was attached by means of stout wires. To this cylinder four rings were attached which supported the paddles. Each ring had eight paddles, and was displaced through a small angle with reference to the one below it, so that no one paddle came over another. By this means the resistance was rendered continuous rather than jerky. The lower rows of paddles were turned backwards, so that they threw the water outwards and kept up the circulation. Around these movable paddles were the stationary vanes, consisting of five rows of ten each. These were attached to the movable paddles by bearings at the extremities of the

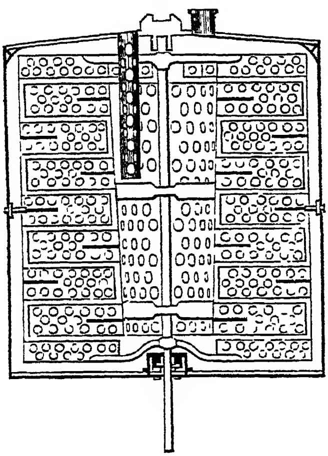

Fig. 163

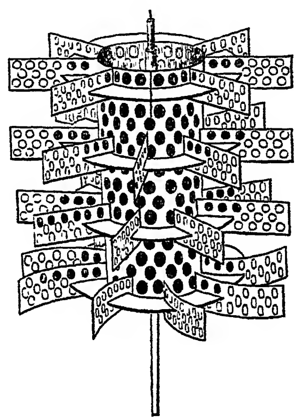

Fig. 164.

shaft, and were removed with the latter when it was taken out of the calorimeter. These outer paddles were fixed to the calorimeter by four screws so as to be stationary.

Two apertures were made in the cover of the calorimeter—one to receive a thermometer, and the other for filling the vessel with water. A copper tube, perforated with large holes, descended from the thermometer aperture, almost to the centre of the calorimeter. The thermometer was contained within this sieve-like tube, with its bulb at a short distance from the centre of the calorimeter, with the revolving paddles outside it and the stream of water circulating around it.

If D denotes the diameter of the torsion wheel, then (p. 583) the work done during n revolutions of the paddle is

$$W = \pi w n D.$$

Hence, if the temperature rises by an amount $\Delta\theta$ (corrected for radiation) in the time occupied by n revolutions, the value of the dynamical equivalent will be given by the equation

$$J = \frac{\pi w n D}{C\Delta\theta},$$

where C is the thermal capacity of the calorimeter and the water contained. To reduce this to absolute measure, we must multiply by $g = 9{\cdot}78009 + 0{\cdot}0508 \sin^2\lambda$ where λ is the latitude of the place. At Baltimore the value is $g = 9{\cdot}8005$ in metres.

The corrections to be applied are—(1) For weighing in air, which must be applied to w and C; if ρ denotes the density of air under the given conditions, this correction amounted to $-0{\cdot}835\rho$. (2) For the weight of the tape by which the torsion weights were suspended; this amounted to $0{\cdot}0006/w$. (3) For the expansion of the torsion wheel; if D' be its known diameter at 20°, then its diameter at any other temperature θ was $D' + 0{\cdot}000018D'(\theta - 20)$. The corrected formula was then

$$J = \frac{\pi n w D' g}{C\Delta\theta}\left\{1 + 0{\cdot}000018(\theta - 20) + \frac{0{\cdot}0006}{w} - 0{\cdot}835\rho\right\}.$$

Owing to the rapid rise of temperature (generally about 0°·6 per minute) the correction for radiation was proportionately small. This correction was $0{\cdot}0014\theta°$ per minute, where θ is the difference of temperature between the calorimeter and its jacket. This amounts to 1 per cent for 10°·7, and to 4 per cent for 14°·2. Generally the calorimeter was cooler than the jacket at the outset, and so an elevation of 20° could be obtained in the temperature of the calorimeter without a rate of correction of more than 4 per cent at any point, and an average correction of less than 2 per cent. An error of 10 per cent was therefore required in the estimation of the radiation to produce an average error of 1 in 500, or an error of 1 in 250 at a single point. The radiation correction was estimated by allowing the calorimeter to cool while the paddles were slowly turned, the work done being allowed for. The losses of heat placed under this head include conduction and convection as well as radiation proper, and were made up as follows:—

Conduction along shaft . . .	·00011
,, ,, suspending wires	·00006
True radiation	·00017
Convection	·00106
Total	·00140

Among the corrections to be applied to the temperature as read off from the thermometer that arising from the unequal temperature of the stem was the greatest and most difficult to estimate. The other corrections arise in pressure on the bulb, conduction along the stem, and the fact that the thermometer is always behind the calorimeter as the temperature of the latter changes.

The following table gives Professor Rowland's results in kilogrammemetres at Baltimore:—

Air Thermometer.	Equivalent.	Air Thermometer.	Equivalent.	Air Thermometer.	Equivalent.
°		°		°	
5	429·8	16	427·2	27	425·6
6	429·5	17	427·0	28	425·6
7	429·3	18	426·8	29	425·5
8	429·0	19	426·6	30	425·6
9	428·8	20	426·4	31	425·6
10	428·5	21	426·2	32	425·6
11	428·3	22	426·1	33	425·7
12	428·1	23	426·0	34	425·7
13	427·9	24	425·9	35	425·8
14	427·7	25	425·8	36	425·8
15	427·4	26	425·7	...	.

To reduce to latitude of Manchester and Berlin 0·5 must be subtracted, and for Paris 0·4.

For the sake of comparison with his own determinations, Professor Rowland also reduced Joule's results to the air thermometer and the latitude of Baltimore, as in the following table:—[1]

Temperature.	Joule's Value.	Joule's Value reduced to Air Thermometer and Baltimore.		Rowland's Value.
		English Measure.	C.G.S. System.	
°				
9	772·8	779·2	427·5	428·8
9	775·4	781·4	428·7	428·8
9	776·0	782·2	429·1	428·8
9	773·9	780·2	428·0	428·8
12·7	774·6	778·5	427·1	428·0
14	772·7	778·0	426·8	427·7
14·5	767·0	770·5	422·7	427·5
14·7	772·7	776·1	425·8	427·6
15·5	773·1	776·4	426·0	427·3
17·3	774·0	777·0	426·3	426·9
18·6	..	.	428·0	426·7

Combining these results, he deduces the value 426·75 at 14°·6 C. from Joule's experiments, and 427·52 from his own. The difference amounts to only 1 in 550, and might arise from variations in the specific heat of water.

280. Miculescu's Experiments.—Quite recently M. Miculescu[2]

[1] *Proc. American Acad. of Arts and Sciences*, vol. viii. (New Series), pt. i. p. 44, 1880-81.

[2] M. C. Miculescu, *Ann. de Chimie et de Physique*, 6e, tom. xxvii. p. 202, October 1892.

has also adopted the friction balance method of determining the dynamical equivalent of heat. In the investigations of Joule and Professor Rowland the axis of the rotating paddle was vertical, passing through the lid of the calorimeter in Joule's apparatus, and through the bottom in Professor Rowland's. In the apparatus adopted by M. Miculescu, on the other hand, the axis of the paddle was horizontal. The work was supplied by a motor supported on a wooden frame, which was suspended from a horizontal axis, round which it could swing freely; and this axis coincided geometrically with the rotating axis of the paddle. With this arrangement the suspended frame, when the apparatus was in motion, tended to incline itself to the vertical in a direction opposite to that of the rotation. It was brought back into its position of equilibrium by a couple of known moment, and the motor thus played the part of its own dynamometer, the work being measured as before (p. 583).

The heat generated was measured by the method of *stationary temperature.* Around the calorimeter (which was fixed independently of the oscillating frame), and through the water in which the paddles turn, a current of cold water circulated in such a way that the temperature of the calorimeter remained fixed. The heat developed in any time was consequently determined by the weight of water which passed through the apparatus in the same time.

The calorimeter was composed of four concentric cylinders—the exterior pair of brass, and the interior pair of copper. The interior or first cylinder contained the revolving paddles, and the exterior or fourth was covered on the outside with felt 1 cm. thick. The first, second, and third cylinders were insulated from each other by pieces of ebonite; and, while a current of water passed through the space between the first and second, the space between the second and third contained air, and the space between the third and fourth was filled with water, and formed a water jacket.

The difference of temperature of the water on entering and on leaving the calorimeter was measured by means of a thermoelectric couple, one junction being situated in the entry and the other in the exit tube. The radiation correction was negligible.

Taking the specific heat of water to be unity between 10° and 13° C., the mean result of these experiments gave the number 426·7; or when temperatures were referred to the hydrogen thermometer, the result was

$$J = 426{\cdot}84.$$

The advantage claimed for this investigation is that all the measurements are made by the *null* method.

281. Remarks on the Various Methods of Determining the Dynamical Equivalent.—Of the various methods of determining the value of the dynamical equivalent of heat, the method of fluid friction is by far the most reliable. The experiments described above are all designed on this principle; but in addition to these accurate investigations many others have been carried out by methods of considerable interest though of less precision.

An indirect method depending on the theory of gases has been already noticed (p. 255); but this method is at best very imperfect, for a small error in the determination of the ratio of the specific heats will produce a considerable change in the value of J. Another method, depending on the assumption that all the work employed in compressing a gas is spent in raising its temperature, has also been adopted. In applying this method Joule[1] forced air into a strong receiver kept under water in a calorimeter, so that the heat developed during the compression could be measured by the change of temperature of the calorimeter. The work spent during the compression was easily calculated on the assumption that air obeys Boyle's law throughout the range of the experiment (see p. 602), and the materials for the determination of J are thus at hand. Instead of compressing the gas and measuring the heat developed, the reverse process may be employed. The gas may be first compressed into a receiver, from which it can be subsequently allowed to escape into the atmosphere, and the cooling produced by the expansion against the external pressure may be measured. Both methods were employed by Joule, who obtained 823 and 795 foot-pounds by the compression process, and 820, 814, 760 by expansion.

Before any inference can be made as to the equivalence of the work done and the heat developed in such a process, it must be ascertained that the whole work is spent in generating heat, and that no part of it is employed in altering the state of the substance, or, in other words, in doing internal work. For this reason Joule felt compelled to execute those experiments (p. 250) by which he proved that no appreciable internal work is done during the compression or expansion of a gas. The only reliable mode of procedure, therefore, is to adopt a method in which the state of the substance is the same at the end of the operation as at the beginning. This holds good in all fluid friction methods which are consequently much superior to all methods depending on compression, or expansion, or percussion.

An interesting determination of J by estimating the heat developed by percussion in a mass of lead was made by Hirn.[2] Lead was chosen

[1] Joule, *Phil. Mag.*, 3rd Series, vol. xxiii., 1845; *Scientific Papers*, p. 172.

[2] Hirn, *Théorie Mécanique de la Chaleur*, tom. i. p. 96, 3rd ed.

because it is highly inelastic. It is for this reason that when a leaden bullet strikes a target (or is struck), nearly all the energy of motion is converted into heat. In addition, lead when struck yields but little sound, and its state is not appreciably altered by hammering. Elastic bodies, on the other hand, when they collide, rebound and regain a large proportion of their original energy, so that but little heat is generated by the impact. The apparatus devised by Hirn is shown in Fig. 165.

A cylinder of iron AA weighing 350 kilos was suspended, with its axis horizontal, by two pairs of cords which compelled it to move in a vertical plane with its axis always horizontal. This cylinder was used as the hammer or instrument of percussion. The anvil MB was a large prismatic mass of stone weighing 941 kilos, and suspended in

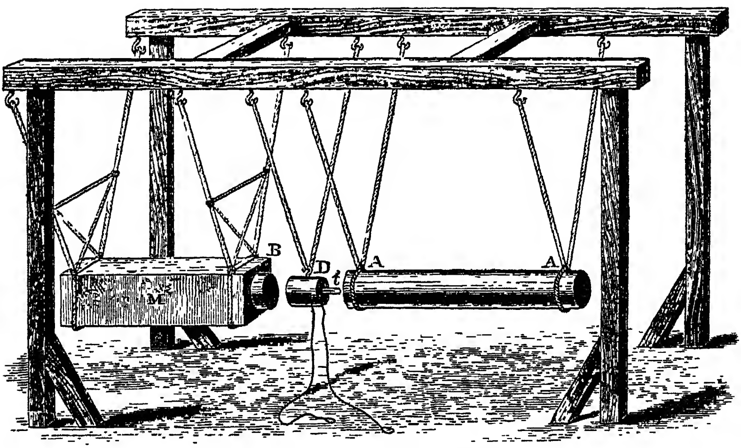

Fig. 165.—Hirn's Percussion Apparatus.

the same way as the hammer. The mass of lead D to be operated on was suspended between the two, and the face B of the anvil adjacent to the lead was cased with iron to receive the blow.

In making an experiment the hammer was drawn back by a tackle, and the height to which it was raised was accurately measured. It was then let fall upon the lead, and the recoil of the anvil was registered by a sliding indicator which was pushed back and then remained *in situ*. An observer also noted the advance or recoil of the hammer after the blow, and from these data the work spent in percussion could be easily calculated. Before the blow was delivered the temperature of the lead was taken by inserting a thermometer *t* into a cylindrical cavity made in the mass, and immediately after the blow the mass of lead was removed and hung up by two strings provided for the

purpose, so that the axis of the cavity was vertical. This cavity was immediately filled with ice-cold water, which was stirred and the rise of temperature noted. The value 425 kgm. was obtained by Hirn in this manner, which is remarkably good considering the nature of the experiment. The following details will illustrate the method:—

Height of fall of hammer . .	1·166 m.
Recoil of hammer	0·087 m.
,, of anvil . . .	0·103 m.
Weight of lead .	2·948 kg.
Temperature before blow .	7°·873
,, four minutes after .	12°·1
,, eight minutes after .	11°·75
,, of air . . .	8°·8
Weight of water placed in cavity . .	0·0185 kg.

An indirect method depending on the theory of saturated vapours (p. 652) has also been employed, but on account of the difficulty of experimentally determining the densities or specific volumes of saturated vapours, this method is better suited for the calculation of vapour densities from the knowledge of the value of J than for the calculation of the latter quantity.

Other indirect methods have also been employed which depend upon electric, or electromagnetic, or capillary, phenomena. When an electric current of strength C passes through a wire of resistance R, the heat developed in a time t is determined by the equation

$$JH = C^2Rt,$$

and when C, R, and H are measured, the value of J can be deduced. The principal difficulty attending this method is that of determining R in absolute measure. Further, the temperature of the wire must be higher than that of the calorimeter, so that the heat developed in the wire will be greater than that calculated, and the value of J determined will consequently be too small.

This difficulty, however, appears to have been surmounted by Mr. E. H. Griffiths,[1] who has recently proved that the method is capable of yielding exceedingly good results, the electrical units having now been determined with sufficient accuracy.[2] The calorimeter was suspended within an air-tight steel chamber. The walls and floor of this chamber were double, and the space between them was filled with mercury. The calorimeter was thus practically suspended within the bulb of a huge thermometer (70 lbs. of mercury), a change of 1° C. causing the mercury to rise 300 mm. in the tubes of the

[1] E. H. Griffiths, *Proc. Roy. Soc.*, vol. liii. p. 6, 1893.
[2] *Brit. Assoc. Report*, 1892.

regulating apparatus. By special arrangements the walls surrounding the calorimeter could be maintained for any length of time at any required temperature from that of the water-taps to 40° or 50° C. The space between the calorimeter and the walls of the steel chamber was exhausted to a pressure of less than 1 mm., and a sudden decrease in the loss of heat by radiation was observed when the pressure fell below 0·5 mm., as previously noticed by Dr. Bottomley[1] (p. 462). The terminals of the calorimeter resistance coil (platinum wire) were kept at a constant difference of potential by means of Clark's cells and an adjustable resistance in the battery circuit. The value of J deduced in this manner was 427·45 k gramme-metres in the latitude of Greenwich (g. = 981·17), the specific heat of water at 15° C. being unity, and at any other temperature $1 - 0{\cdot}000266\ (\theta - 15)$.

The heat developed in a copper disc when rotated in a magnetic field also furnishes a method of evaluating J, but the heat lost while the disc is rotating and while it is being transferred to the calorimeter must lead to uncertain corrections. This method was used by M. Violle in 1870. Other methods, such as the steam-engine experiments of Hirn (p. 48), and those of Edlund on the expansion and contraction of metals, are excellent as illustrations of the dynamical theory, but they cannot be regarded as possessing any accuracy. The chemical action which takes place in a voltaic battery or in a voltameter also furnishes a method of determining J.

The dynamical equivalent of heat has also been determined experimentally by the change of temperature produced when a liquid escapes under pressure from an orifice, or when a liquid is forced through capillary tubes. By the escape of water under pressure Hirn found the value 433 kgm., and by forcing water through a piston perforated with small holes Joule obtained the number 770 foot-pounds.

The following table contains the results obtained by the various methods :—

[1] *Phil. Trans.*, 1887, A.

[TABLE

Direct Methods

Date.	Observer.	Method.	Result.
1843	Joule (1)	Friction of water in tubes	424·6
,,	,,	Electromagnetic currents	460
,,	,,	Decrease of heat produced by a pile when the current does work . .	442·2
1845	,,	Compression of air . . .	443·8
,,	,,	Expansion of air	437·8
,,	,,	Friction of water in a calorimeter .	488·3
1847	Joule (2)	,, ,, ,, . .	428·9
1850	,,	,, ,, ,, .	423·9
,,	,,	Friction of mercury in a calorimeter .	424·7
,,	,, (3)	Friction of iron plates in a calorimeter	425·2
1857	Favre (4)	Decrease of heat produced by a pile doing work	426-464
,,	Hirn (5)	Friction of metals .	371·6
1858	,,	,, ,, ...	400-450
,,	Favre (6)	Friction of metals in mercury calorimeter	413·2
,,	Hirn (5)	Boring of metals	425
1860-61	,,	Water in friction balance	432
,,	,,	Escape of liquids under high pressure .	432, 433
,,	,,	Hammering lead	425
,,	,,	Friction of water in two cylinders .	432
,,	,,	Expansion of air	440
,,	,,	Steam-engines	420-432
1865	Edlund (7)	Expansion and contraction of metals .	428·3-443·6
1870	Violle (8)	Heating of a disc between the poles of a magnet	435
1875	Puluj (9)	Friction of metals	425·2-426·6
1878	Joule (10)	,, water	423·9
1879	Rowland (11)	,, water between 5° and 36° .	429·8-425·8
1891	D'Arsonval (12)	Heating of a cylinder in a magnetic field	421-427
1892	Miculescu (12a)	Friction of water	426·84

Indirect Methods

Date.	Observer.	Method.	Result.
1842	Mayer (13)	By the relation $J=\dfrac{p_0v_0a}{C_p-C_v}$ for gases .	365
1857	Quintus Icilius (14)	Heat developed in a wire of known resistance	399·7
,,	Weber (15)	Heat due to electric currents .	432·1
,,	Favre / Silberman	Heat developed by zinc on sulphate of copper	432·1
,,	Bosscha (16)	Measure of E.M.F. of a Daniell's cell after the absolute measure 10257×10^7	432·1
1859	Joule (17)	Heat developed in a Daniell's cell .	419·5
,,	Bosscha	E.M.F. of Daniell's cell	419·5
,,	Lenz-Weber	Heat developed in wire of known resistance	396·4-478·2
1867	Joule (18)	Heat developed in wire of known resistance	429·5
1878	Weber	Heat developed in wire of known resistance	428·15
1888	Perot (19)	By the relation $L=\tau\,(v_2-v_1)\dfrac{dp}{dt}$.	424·63
1889	Dieterici (20)	Heat of electric currents	432·5
1893	Griffiths (21)	,, ,, ...	427·45

REFERENCES TO FOREGOING TABLES

(1) Joule, *Phil. Mag.*, 3rd Series, vols. xxiii. and xxvi.
(2) ,, ,, ,, ,, xxvii.
(3) ,, *Phil. Trans.*, p. 61, 1850.
(4) Favre, *Comptes Rendus*, tom. xlv. p. 56.
(5) Hirn, *Théorie Mécanique de la Chaleur.*
(6) Favre, *Comptes Rendus*, tom. xlvii. p. 337.
(7) Edlund, *Pogg. Ann.*, vol. cxiv.
(8) Violle, *Ann. de Chimie et de Physique*, tom. xxi.
(9) Puluj, *Sitzungsberichte der k. Acad. der Wissenschaften in Wien*, 1875; March, p. 667; June, p. 53.
(10) Joule, *Phil. Trans.*, p. 365, 1878.
(11) Rowland, *Proc. American Acad.*, p. 75, 1879-80.
(12) D'Arsonval, *Lumiere Électrique*, March 1891.
(12a) Miculescu, *Ann. de Chimie*, 6e, tom. xxvii. p. 202, 1892.
(13) Mayer, *Liebig's Annalen*, vol. xlii.
(14) Quintus Icilius, *Pogg. Ann.*, vol. ci. p. 69.
(15) Weber, *Phil. Mag.*, 4th Series, vol. xxx.
(16) Bosscha, *Pogg. Ann.*, vol. cxviii. p. 162.
(17) Joule, *Brit. Ass. Rep.*, 1873, p. 175.
(18) Joule, *Phil. Trans.*, 1850, p. 61.
(19) Perot, *Journal de Physique*, 2e, tom. vii. p. 129.
(20) Dieterici, *Annalen der Physik*, vol. xxxiii. p. 417
(21) Griffiths, *Proc. Roy. Soc.*, vol. liii. p. 6, 1893.

SECTION II

THE FIRST FUNDAMENTAL PRINCIPLE

282. The First Law and the Energy Equation.—The modern science of thermodynamics is based on two fundamental principles, both of which relate to the conversion of heat into work. The first of these is the principle of equivalence established by Joule, and is represented algebraically by the equation

$$W = JH.$$

This principle, which is known as the *first law of thermodynamics*, asserts that when work is spent in producing heat, the quantity of work spent is directly proportional to the quantity of heat generated, and conversely, that when heat is employed to do work a quantity of heat disappears which is the equivalent of the work done. This conception is derived from the dynamical theory, according to which heat is regarded as a form of energy, and consequently, when work is done by thermal agencies, or heat generated by the expenditure of work, the quantity expended of either is the equivalent of the quantity generated of the other in accordance with the general principle of the conservation of energy.

Let us now consider the various departments in which a quantity of heat, when communicated to any body, may expend itself. In the first place, a portion of it, but not necessarily all, may be employed in raising the temperature of the body. This portion is spent according to the dynamical theory in increasing that energy known as the sensible heat of the body. The increase of temperature is in general accompanied by increase of volume, and as a consequence work will be expended in two departments. For if the body be subject to external forces, work will be done by or against these forces while the volume is changing. This is termed the *external work*. For example, if the body be subject to a uniform pressure p, the work done against this external pressure during an expansion dv will be pdv. So also work will be done against internal forces, such as molecular attractions; while the

volume or state is changing, and the amount of heat expended in the performance of this, *internal work* as it is called, may be a considerable portion of the whole. Under the head internal work may also be placed the first-mentioned increase of molecular energy or increase of sensible heat of the body.

Thus if the internal energy of the body be denoted by U, and if this embraces both the kinetic and potential energies of the molecules, the heat supplied to the body will be expended in two departments—one in doing external work, and the other in altering the internal energy of the body. Hence, if the external work done is dW, and if the change of internal energy is dU, when a quantity of heat dQ is given to a body, we have

$$dQ = dU + dW \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The symbol J being avoided by expressing dQ in work units (ergs).

The quantity of heat dQ is regarded as positive when given to the body, and negative when taken from it. Under these circumstances the work dW must be regarded as positive when done by the body, and negative when done on it, in accordance with equation (1). When the external work is introduced by ordinary mechanical reactions, resistance to distortion, etc., the expression for dW takes the usual form of stress multiplied by strain, but work may be done by a system in many other ways. For example, a liquid, in altering the area of its surface, is subject to capillary forces, and if T denotes the surface tension, and dS an element of surface, the expression for dW in this case is TdS. So also work may be done in consequence of electric or magnetic forces when electrified or magnetised matter is moved from places of lower to places of higher potential. Thus, if a quantity dq of electricity is moved from a place of zero potential to a place at potential V, the expression for dW is Vdq. If, however, energy be given to external systems only by work done against a uniform normal pressure p, then $dW = pdv$, and the energy equation becomes

External work.

$$dQ = dU + pdv \quad . \quad . \quad . \quad . \quad . \quad (2)$$

283. Remarks on the Energy Equation—Cyclic Transformations. —In general for every substance there is some characteristic equation connecting the volume, pressure, and temperature, so that when any two of these quantities are known, the third is completely determined. For this reason, when the condition of a substance is represented graphically, as in Art. 69, the pressure and volume being known, the temperature corresponding to any point A (Fig. 166) becomes

determinate, and the state represented by the point is unique.[1] Hence we may assume that the internal energy U, which appears in the energy equation, is completely determined for any state by the co-ordinates of the point which represents that state in the diagram.

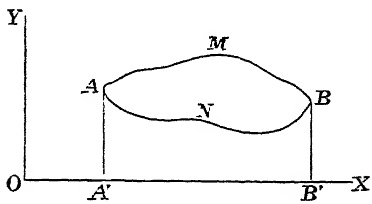

Fig. 166

This is expressed by saying that the internal energy U corresponding to any state A is a function of the co-ordinates which define the state, and consequently the change of internal energy in passing from any state A to another state B will depend only on the points A and B, and in no way on the nature of the transformation by which the body may pass from A to B. In other words, if a substance be brought from any state A to any other state B, through any series of transformations represented by the path AMB, the change of internal energy depends only on the co-ordinates of A and B, being independent of the nature of the path AMB. The assumption made here is merely that if a body, after passing through any series of transformations, be brought back again to its initial condition, its internal energy will be the same at the end of the cycle as at the beginning, whether it returns to its initial condition by the same path, AMB, as it set out, or by a different, ANB. This amounts to saying that U at any point is a single valued function of the co-ordinates of the point, or that dU is *a perfect differential.*

On the other hand, the external work done during any transformation depends not only on the initial and final conditions of the substance, but also on the nature of the intermediate operations. For, as has been shown (Art. 69), the external work performed in passing from the state A to the state B along the path AMB is represented by the area AMBB′A′, so that the external work is not known unless the shape of the curve AMB, or the relation connecting the volume and pressure throughout the transformation, is known. In other words, W is not determined by the initial and final co-ordinates, and dW *is not a perfect differential.* The work done during any transformation depends on the nature of the transformation from beginning to end, and in order to estimate it we require not only a knowledge of the

[1] An ambiguity arises when more than one value of the temperature can exist for the same values of the pressure and volume; so also in the case of a liquid and its saturated vapour, the pressure is a function of the temperature alone, and the volume within certain limits is independent of both.

initial and final states, but also some subsidiary relation, such as $f(p,v)=0$, connecting the volume and pressure throughout the transformation.

It thus appears that the quantity of heat supplied to a body in passing from the state A to the state B depends on the nature of the transformation by which it is brought from A to B as well as on the positions of these points. This quantity of heat consequently cannot be expressed, like the internal energy, in terms of the co-ordinates of A and B, but requires a knowledge of the subsidiary relation $f(p,v)=0$, that is the shape of the path AMB. Hence dQ *is not a perfect differential.* In the language of the differential calculus this is expressed by saying that, in the case of the internal energy U, we have

$$\frac{d}{dx}\left(\frac{dU}{dy}\right)-\frac{d}{dy}\left(\frac{dU}{dx}\right)=0,$$

where x and y are the independent variables chosen to determine the condition of the body. But in the case of the quantity of heat Q, we have

$$\frac{d}{dx}\left(\frac{dQ}{dy}\right)-\frac{d}{dy}\left(\frac{dQ}{dx}\right)\gtrless 0.$$

According to the caloric theory, however, which regarded heat as indestructible, the quantity of heat supplied to a body in passing from any state A to any other state B must depend only on the initial and final states, and not on the nature of the intermediate transformations. According to this theory, then, dQ would be a perfect differential, and the external work would be derived from the heat, not by using up an equivalent quantity of it, but by transferring it, unaltered in quantity, from bodies of higher to bodies of lower temperatures, in a manner somewhat analogous to the way in which work is obtained by allowing water to descend from places of higher to places of lower level.

The fact that dQ is not a perfect differential according to the dynamical theory arises therefore from the principle of equivalence, according to which, when any substance passes through any cycle of transformations, an amount of heat disappears which is the equivalent of the work done, and if the substance be brought back to its initial condition after passing through a complete cycle of transformation, a quantity of heat represented by the area of the cycle is destroyed, or generated, according to the direction in which the cycle is passed through.

284. Integrating Factor of the Energy Equation.—If x and y be any two independent variables which determine the condition of a body, it follows that dQ may be expressed in the form

$$dQ=Xdx+Ydy. \qquad (1)$$

where X and Y are each functions of x and y; but since dQ is not a perfect differential, dX/dy will not be equal to dY/dx. The left-hand side of this equation may, however, be made an exact differential by multiplying it by a factor μ, which is some function of x and y. The quantity μdQ will then be a perfect differential, and we shall consequently have

$$\frac{d}{dx}\left(\mu Y\right)=\frac{d}{dy}\left(\mu X\right),$$

or

$$\mu\left(\frac{dY}{dx}-\frac{dX}{dy}\right)=X\frac{d\mu}{dy}-Y\frac{d\mu}{dx},$$

an equation which expresses the integrating factor μ in terms of X and Y.

The relation between X and Y may be deduced by comparing (1) with the energy equation. For since U and W are supposed expressible in terms of x and y, we have

$$dU=\frac{dU}{dx}dx+\frac{dU}{dy}dy, \text{ and } dW=X'dx+Y'dy.$$

But by the energy equation we have

$$dQ=\left(\frac{dU}{dx}+X'\right)dx+\left(\frac{dU}{dy}+Y'\right)dy,$$

and therefore

$$X=\frac{dU}{dx}+X', \text{ and } Y=\frac{dU}{dy}+Y'.$$

Hence, since dU is a perfect differential, it follows that we must have

$$\frac{d}{dx}\left(Y-Y'\right)=\frac{d}{dy}\left(X-X'\right),$$

or

$$\frac{dY}{dx}-\frac{dX}{dy}=\frac{dY'}{dx}-\frac{dX'}{dy}.$$

In the particular case when the only external force is a uniform normal pressure p, and in which the independent variables which determine the condition of the body are p and v, we have

$$dQ=Ldv+Mdp,$$

where L is the heat of dilatation or the quantity of heat absorbed by the body under constant pressure, while its volume changes by unity, and M is the quantity of heat required to change the pressure by unity when the volume is kept constant. Hence if μ is the integrating factor

$$\frac{d}{dp}\left(\mu L\right)=\frac{d}{dv}\left(\mu M\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But by the energy equation

$$dQ = \frac{dU}{dp}dp + \frac{dU}{dv}dv + pdv.$$

Therefore

$$L = \frac{dU}{dv} + p, \quad \text{and } M = \frac{dU}{dp}.$$

Hence, since U is a perfect differential, we have

$$\frac{dL}{dp} - \frac{dM}{dv} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

as the relation between L and M.

Using this result equation (2) becomes

$$\mu = M\frac{d\mu}{dv} - L\frac{d\mu}{dp},$$

which expresses μ in terms of L and M.

COR. In the case of a perfect gas an integrating factor is the reciprocal of the temperature Θ measured from the zero of the perfect gas thermometer. For in the case of a perfect gas the energy equation is (Art. 144)

$$dQ = C_v d\theta + pdv.$$

Therefore

$$\frac{dQ}{\Theta} = C_v\frac{d\theta}{\Theta} + R\frac{dv}{v},$$

and the right-hand member of this equation is obviously an exact differential. Hence dQ/Θ is a perfect differential.

Examples

1. If there is one integrating factor of dQ, show that there are an infinite number.

[If μ is an integrating factor of dQ, then

$$\mu dQ = d\phi.$$

But if Φ be any function of ϕ, we have

$$\Phi = f(\phi), \quad \text{and } d\Phi = f'(\phi)d\phi,$$

consequently

$$\mu f'(\phi)dQ = f'(\phi)d\phi = d\Phi,$$

so that the factor $\mu f'(\phi)$ also renders dQ a perfect differential.]

2. Denoting the specific heats at constant pressure and constant volume by C_p and C_v respectively, prove that in dynamical units

$$C_v = \left(\frac{dU}{d\theta}\right)_v, \quad \text{and } C_p = \left(\frac{dU}{d\theta}\right)_p + p\frac{dv}{d\theta}.$$

[Since U is completely determined by the variables v and θ, we have

$$dQ = \left(\frac{dU}{d\theta}\right)_v d\theta + \left(\frac{dU}{dv}\right)_\theta dv + pdv.$$

Hence, as is otherwise directly obvious,

$$\left(\frac{dQ}{d\theta}\right)_v = C_v = \left(\frac{dU}{d\theta}\right)_v,$$

and similarly by taking p and θ as independent variables we obtain the second relation.

In the case of a perfect gas U is a function of θ alone, and hence

$$\left(\frac{dU}{d\theta}\right)_p = \left(\frac{dU}{d\theta}\right)_v = C_v,$$

so that the second relation becomes $C_p - C_v = R$.]

3. A gas changes its volume from v_1 to v_2, at constant temperature, find the quantity of heat absorbed.

[Since the temperature is constant the energy equation $dQ = C_v d\theta + pdv$ becomes

$$dQ = pdv = R\Theta\frac{dv}{v}.$$

Hence the heat absorbed is (in dynamical units)

$$Q = R\Theta \log (v_2/v_1).$$

From this relation it follows that if the isothermal changes of a gas are such that the quantities of heat absorbed or evolved form an arithmetical progression, the corresponding changes of volume form a geometrical progression.[1]

The above equation may also be written in the form

$$Q = p_1 v_1 \log (v_2/v_1),$$

so that if this refers not to unit mass of the gas, but to that quantity which assumes a volume v_1 under a pressure p_1, the equation contains nothing depending on the nature of the gas. This equation was employed by Joule in one of his determinations of J.]

4. Determine the work done when a gas is compressed adiabatically from $p_1 v_1$ to $p_2 v_2$.

[We have

$$W = \int pdv = p_1 v_1^{\gamma} \int \frac{dv}{v^{\gamma}} = \frac{p_1 v_1}{\gamma - 1}\left\{1 - \left(\frac{v_1}{v_2}\right)^{\gamma - 1}\right\} = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1}.\ ]$$

5. Prove that the areas included between the adiabatic lines of a perfect gas and the axis of volume are equal if measured from the points where they are intersected by any isothermal.

[This follows from the property that the internal energy of a perfect gas is a function of the temperature only.]

6. If μ is an integrating factor of dQ, prove that taken round any closed cycle

$$\int \mu dQ = 0.$$

[Since $\mu dQ = d\phi$, it follows that the value of the integral taken along any curve joining two points $p_1 v_1$ and $p_2 v_2$ is simply $\phi_1 - \phi_2$ where ϕ_1 is the value of ϕ at $p_1 v_1$, and ϕ_2 its value at $p_2 v_2$. When the cycle is closed $\phi_1 = \phi_2$.]

7. If a substance has attained its maximum density under a given pressure, prove that the tangent plane to the characteristic surface at the corresponding point is parallel to the axis of temperature.

[1] This result was arrived at by Carnot, *Motive Power of Heat*, p. 81, English edition.

[If the characteristic equation be $f(p, v, \theta)=0$, then under constant pressure we have

$$\frac{df}{d\theta}+\frac{df}{dv}\frac{dv}{d\theta}=0.$$

But if the density is a maximum $dv/d\theta=0$; therefore at the corresponding point we have $df/d\theta=0$, which was to be proved.

The locus of these points is a curve on the characteristic surface which obviously divides it into two parts, such that the projection of one on the plane pv is the same as that of the other. Hence it follows that every curve on the characteristic surface which cuts this locus projects on the plane pv into a curve touching the projection of the locus, and consequently two curves which intersect on it project into two which touch each other.]

SECTION III

THE SECOND FUNDAMENTAL PRINCIPLE

285. The Work of Sadi Carnot.—At the time when Sadi Carnot wrote his celebrated essay (1824) on "The Motive Power of Heat,"[1] the works of Rumford and Davy had been completed, and the undulatory theory of light was regarded as established by weighty arguments in every department, yet the caloric theory of heat still held its ground, and the scientific world remained to be converted to the new doctrine. The introduction of the steam-engine, and the great industrial revolution which accompanied it, attracted attention to the manner in which work may be produced by heat; and it was in seeking to discover the general laws which govern the action of heat-engines, that Carnot was led to some of those forms of reasoning which are still continually employed in the dynamical theory.

Before the time of Carnot no relation seems to have been suspected between the work performed by a steam-engine and the heat drawn from the furnace. In seeking to establish this relation Carnot based his work on the doctrine of the conservation of energy, or the impossibility of perpetual motion; and although in conjunction with this he espoused the doctrine of the conservation of caloric, yet in much of his work the latter is not essential, and many of his conclusions remain true on any theory and require but little modification to adapt them to the dynamical theory. It is, besides, in this work that we find the first examples of cyclic operations in which a working substance, after passing through any series of transformation, is brought back again to its initial condition; and it is only for such a cycle, Carnot informs us, that we are entitled to reason upon the relation between the external work done and the heat employed in its production.

In fact, as we have already mentioned, if a substance be allowed to

[1] Sadi Carnot, *Réflexions sur la puissance motrice du feu et sur les moyens propres à la développer* (translated recently by R. H. Thurston, 1890. London: Macmillan and Co.).

expand, doing external work, it is not legitimate to assert that the heat spent is the equivalent of the work done unless the substance in its final state is in exactly the same condition as at the beginning; but when the substance has been brought back to its initial state, we are entitled to assert that, on the whole, it has neither lost nor gained energy, and we are then in a position to reason upon the external processes that have taken place, and to determine the condition of equivalence among them.

Besides this conception of complete cycles, the other grand idea introduced by Carnot was the principle of reversibility—namely, that by the expenditure of an equal quantity of work the heat may be taken from the condenser and restored again to the source.

In spite of his adoption of the caloric theory,[1] Carnot seems to have been by no means confident of its truth, and in his later writings (which unfortunately remained unpublished until recent times) he showed that he was thoroughly convinced that it was false, as he not only espoused the dynamical theory, but also planned several experiments to determine the equivalent relation between heat and work, and deduced a value of that equivalent probably from the very data employed by Mayer in 1842. That Carnot was finally convinced of the truth of the dynamical theory, and that he had also conceived the great principle of the conservation of energy in its general form, is distinctly proved by the following passages taken from his notes, written when the wave theory of light had just triumphed:—

"At present light is generally regarded as a vibratory motion of the ethereal fluid. Light produces heat, or at least accompanies the radiating heat, and moves with the same velocity as heat. Radiating heat is then a vibratory movement. It would be ridiculous to suppose that it is an emission of matter while the light which accompanies it could be only a movement.

"Could a motion (that of radiating heat) produce matter (caloric)?

"No, undoubtedly; it can only produce a motion. Heat is then the result of a motion.

"It is then plain that it could be produced by the consumption of motive power, and that it could produce this power.

"Heat is simply motive power, or rather motion which has changed form. It is a movement among the particles of bodies. Wherever there is a destruction of motive power, there is at the same time production of heat in quantity exactly proportional to the quantity of motive power destroyed. Reciprocally, whenever there is destruction of heat, there is production of motive power.

"We can then establish the general proposition that motive power is in quantity

[1] It is interesting to note that of the two principles adopted by Carnot, viz. the impossibility of perpetual motion and the conservation of caloric, the former was by no means generally received at the time, while the latter was generally admitted as true. At present the former is universally admitted as true, while the latter is as generally believed to be false.

invariable in nature—that it is, correctly speaking, never either produced or destroyed. It is true that it changes form—that is, it produces sometimes one sort of motion, sometimes another, but it is never annihilated."

These words prove that some time before his death (in 1832) he was not only convinced of the truth of the dynamical theory of heat, but that he had also grasped the law of conservation of energy in its widest form. "Motive power," he says, "is in quantity invariable in nature; it is, correctly speaking, never either produced or destroyed."

Working on the caloric theory, however, he postulated that in the steam-engine and other heat-engines the work is performed not by an actual consumption of caloric, which was opposed to the doctrine of the materiality of heat, but "to its transportation from a hot body to a cold body." Thus by the fall of heat from a higher to a lower temperature he supposed work to be done in a manner in some way analogous to that in which work is obtained by allowing water to fall from a higher to a lower level. In the latter case the quantity of water which reaches the lower level is the same as that which leaves the higher; none of the water is destroyed in performing any work which it may be employed to do. It is the motion acquired in falling that is used up in doing work. The work derived from a heat-engine was supposed to be produced in a somewhat similar manner, the quantity which reached the condenser being supposed the same as that which left the source. Thus the work was done by the caloric in flowing from a hot to a cold body, and in doing the work it was supposed, like the water, to be wholly or partially brought to rest. This Carnot speaks of as "the re-establishment of equilibrium in the caloric."

One of the chief points, however, is the recognition by Carnot of the necessity in all engines by which work is continuously derived from thermal agencies, of two bodies at different temperatures, that is a source and a condenser, or the passage of heat from one body to another at a lower temperature.

286. Carnot's Cycle.—Carnot's work failed to attract attention until ten years after its publication, when it was brought into prominence by Clapeyron,[1] who cleared up most of what remained obscure in Carnot's reasoning, and exhibited it in a more elegant form by representing the various transformations geometrically by means of indicator diagrams. The cycle which Carnot supposed his working substance to traverse when geometrically represented consists of a four-sided figure, ABCD (Fig. 167), bounded on two opposite sides,

[1] Clapeyron, *Journal de l'École polytechnique*, tom. xiv., 1834. Translated in Taylor's *Scientific Memoirs*, part iii.

AD and BC, by isothermal lines, and on the remaining pair by adiabatic lines.

The working substance is taken in the state represented by the point A, and being contained in a non-conducting vessel, is allowed to expand adiabatically—that is, without thermal communication with other bodies—until it reaches the state B. During this operation external work, represented by the area ABB′A′, is done by the substance, and its temperature falls from θ to θ'. The next operation is an isothermal compression along the curve BC to some arbitrary point C. During this stage work represented by the area BCC′B′ is done on the substance, and as the temperature is supposed to be kept constant, the heat developed by the compression must be removed as fast as it is generated. Let the quantity thus removed be Q′. The third operation is an adiabatic compression of the substance from C to D until the substance regains its original temperature θ, so that D is on the isothermal line which passes through A. During this operation, work, represented by the area CDD′C′, has been done on the substance while its temperature has been raised from θ' to θ. The fourth and last operation is the isothermal compression of the substance from D to the starting-point A. During this transformation the substance expands, doing external work represented by the area DAA′D′, while in order to keep its temperature constant a quantity of heat Q must be absorbed from some external source. This quantity, if no hypothesis be made concerning the nature of heat, may be either equal to or different from the quantity Q′ evolved by the substance during the isothermal compression BC.

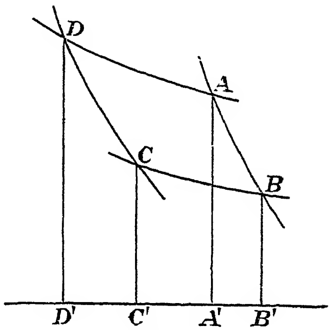

Fig 167.

If the caloric theory be admitted, then Q must be equal to Q′, and regarding the cycle as a whole, an amount of work represented by the area DABB′D′ has been done by the substance, while DCBB′D′ has been done on it, leaving a balance represented by the area of the figure ABCD as the work gained during the cycle.

So far the whole process is independent of any theory of heat,[1] and

[1] The cycle described here is virtually that given by Carnot in his original essay. He begins it with the adiabatic operation AB, and terminates with the isothermal DA. As usually described it would appear as if Carnot's account required correction and modification to adapt it to the dynamical theory. The cycle described by Carnot is

must stand intact whatever theory be adopted. The substance has simply passed through a cycle of operations, and has now returned to its initial condition. If $Q = Q'$, as Carnot taught, the work has been obtained simply by the flow of a quantity Q of heat from a temperature θ to a lower temperature θ'. If, on the other hand, the dynamical theory be adopted, a quantity of heat, equivalent to the work performed during the cycle, must have disappeared. In other words, Q
$Q > Q'$. is greater than Q', and the difference $Q - Q'$ has been converted into work represented by the area of the cycle. This conclusion is in strict accord with all experimental investigation, and the direct verification in the case of the steam-engine has been already noticed (p. 47).

In order to realise such a cycle it would be necessary to enclose the working substance, say a gas, in a non-conducting cylinder fitted with a non-conducting piston and a perfectly-conducting bottom. We must also be provided with two bodies which can be maintained at constant temperatures θ and θ'.

In the first operation the cylinder must be placed on a non-conducting support, and the substance, supposed to be initially at the temperature θ, is allowed to expand without loss or gain of heat until its temperature falls to θ'. The cylinder is then removed from the support and placed with its conducting bottom in contact with the body at temperature θ'. The second operation is now commenced, and the substance is compressed while its temperature is maintained constantly at θ'.

In any actual operation, of course, the temperature of the working substance would exceed that of the body to which it yields its heat, but by compressing very slowly this difference can be made as small as we please. Again, the working substance is supposed to yield its heat to a body constantly at the same temperature θ', and this would require the body to have an infinite capacity for heat, or else to be maintained in some way constantly at the same temperature θ' by internal or external transformations. The second transformation of the cycle is consequently like the first, only an ideal limit which may be approached but not attained in practice. This, however, will not invalidate the adoption of such a cycle in our

independent of all theory; he merely describes a series of transformations through which the working substance passes. It is in the subsequent deductions, founded on some postulate as to the manner in which work is obtained from heat, that the theory comes in. The corrections to Carnot's work introduced by James Thomson and Maxwell are consequently not only unnecessary, but are an injustice to the illustrious author of *The Motive Power of Heat*, and no doubt they were proposed at a time when Carnot's work was learned by report rather than by consultation of the original.

reasoning concerning heat-engines. It merely furnishes us with an ideal type to which we can only approximate in practice.

The third operation is conducted like the first by placing the cylinder on the non-conducting stand and compressing until the original temperature θ is regained. The cylinder is then placed in contact with the other body or source of heat at temperature θ, and the working substance is allowed to expand while heat is supplied to it as required in order to keep its temperature constant.

The characteristic of the cycle, which must be carefully kept in view in order that it may be reversible, is that the working substance parts with heat to, and takes in heat from, bodies at the same temperature as itself. There is no passage of heat by conduction from one body to another at a lower temperature. The transference of heat between the working substance and any other body is such that this substance and the body in question are at the same temperature while the transference is taking place.

Further, all the heat absorbed by the working substance is taken in at one temperature and all the heat given out is ejected at another. There are thus only two temperatures involved, and this renders the cycle the simplest possible representation of a heat-engine, just as the simplest representation of an engine worked by water power would be the case in which the water is all received at one level and all ejected at another —for example, the case of a water wheel in which there is no leakage.

An examination of the foregoing cycle shows that it is *reversible*— that is, if the working substance be made to traverse it in the opposite direction, the operations will be all repeated in the inverse order and opposite sense. Thus a quantity of heat Q will be evolved at θ by the working substance in passing from A to D, and a quantity Q′ will be absorbed at θ' in passing from C to B, while during the complete cycle an amount of work represented by the area of the cycle is done on the substance. In other words, by the expenditure of work a quantity of heat is taken in at the lower temperature θ', and another quantity is evolved at a higher temperature θ, or heat is transported from a cold body to a hot body by the expenditure of work, just as water may be transported from a low level to a higher.

Reversible cycle.

The process by which heat is converted into work is said to be reversible when, if worked backwards (that is, if the cycle of transformations be performed in the inverse order), the physical and mechanical agencies in every part of the cycle are all reversed. The first condition of reversibility, of course, is the possibility of causing the substance to pass back again from its final to its initial state successively, and in the reverse order through all the stages passed through in the direct

process. A *reversible engine* is one in which the working substance passes through a reversible cycle. When it is not possible to repeat the transformations in the reverse order, or when reversed if the agencies are not equal in magnitude and opposite in sign to those which occur at the same point in the direct process, the transformation is said to be *irreversible*.

287. Efficiency of a Reversible Engine—Carnot's Theorem.—If we define the efficiency of a heat-engine as the ratio of the quantity of work W done during a complete cycle to the quantity of heat Q drawn from the source, we can easily show that the efficiency of all reversible engines must be the same, and that this is the major limit to the efficiency of any engine. In other words, no engine can be constructed having an efficiency greater than that of a reversible engine. For let us suppose that it is possible to construct an engine B, which has a greater efficiency than a given reversible engine A. Then if A draws a quantity Q of heat from the source, and performs an amount of work W during each stroke of the piston, it will restore a quantity Q of heat to the source when worked backwards by the expenditure of a quantity of work W, since it is supposed reversible. Now let the engine B draw a quantity Q of heat from the source during each stroke (this can be made the same as the quantity drawn by A by simply altering the quantity of working substance in the cylinder), and let this engine perform, if possible, a quantity of work $W' > W$. Then B may be employed to drive A backwards, and in addition we will have a quantity of work $W' - W$ at our disposal, which can be employed in any manner. Now B draws Q from the source, and A, being worked backwards, restores Q to it. Consequently the compound engine, consisting of A and B working together, furnishes us with a quantity of work $W' - W$ every stroke, while no heat is drawn from the source. According to the caloric theory, the body of lower temperature, that is, the condenser, will also be unaffected, so that we have an engine which would supply us constantly with work without compensation of any kind—that is, we have perpetual motion. In this manner, by assuming the impossibility of perpetual motion, Carnot proved that no engine can have a greater efficiency than a reversible engine. This, then, is the major limit to the efficiency of any heat-engine, and it follows as a corollary that no reversible engine can have a greater efficiency than any other reversible engine; or, in other words, all reversible engines must have the same efficiency.[1]

[1] It is by no means, however, evident *a priori* that the efficiency of a reversible engine should be independent of the nature of the working substance. Thus ether

The same result holds also according to the dynamical theory, when a suitable hypothesis is made concerning the conditions under which work may be derived from heat. Carnot's hypothesis was, as we have already seen, that work is obtained by simply letting heat pass, unaltered in quantity, from a hot body to a cold body. The corresponding hypothesis necessary under the dynamical theory is easily deduced, and was arrived at almost simultaneously by Clausius and Lord Kelvin in slightly different but equivalent forms.

Thus, as before, let us suppose that an engine B is more efficient than some reversible engine A, and let B work A backwards. Then, according to the dynamical theory, the quantity which either draws from the source, when working direct, exceeds that which it yields to the condenser by an amount which is the equivalent of the work done during the cycle. Hence, if A and B be so constructed, by suitably arranging the quantity of the working substance, that they draw the same quantity of heat from the source during each stroke of the piston, then if B does more work than A, it must yield less heat to the condenser, so that when A and B are coupled up (A working backwards) the source will remain unaffected, but A will draw more heat from the condenser than B yields to it. There will thus be a quantity of work $W' - W$ derivable from the compound engine and a corresponding withdrawal of heat from the condenser. This amounts to obtaining work continuously by using up the heat of the colder of two bodies. That this is impossible was the form in which Lord Kelvin stated the hypothesis. In other words, this hypothesis asserts that the manner in which work is derived from heat is by using up the heat of the hotter of two bodies, a quantity Q being drawn from this body, and in part converted into work, while the remainder is yielded to the colder body.

It is not, however, *a priori* evident that work cannot be derived by using up the heat of a single body, or by using up the heat of the coldest of a system of bodies. That all engines which have been constructed to work in complete cycles do work by using up the heat

boils at 35°, and the tension of its vapour at 90° is equal to that of water at 150°, while to produce a gramme of ether vapour requires five times less heat than a gramme of water vapour, therefore ether at the expense of much less heat places a far greater pressure at the disposal of the workman. What compensation does water offer? Carnot was satisfied to assert that any incomplete compensation would be attended by perpetual motion. Without entering into a full discussion of the question, we may state that complete compensation does take place, that although a much greater pressure for the same expenditure of heat is obtained with ether vapour, yet more work cannot be obtained, for work requires expansion, and this produces cooling and consequent condensation, so that in this operation the compensation is effected.

of the hotter body, or source, is true; but if at any time we should obtain the means of dealing with the molecules individually, and not as now in the aggregate, it is not impossible that all the molecular motion of a single body should be used up in doing work, or be transferred to another body, so that work might be obtained by using the heat of a single body or of the coldest body of a system, or all the heat of one body might be transferred to another at a higher temperature.

Another method of regarding the question leads to the form in which the hypothesis was stated by Clausius. Thus we have seen that in Carnot's cycle work can be performed by drawing heat from a source and giving at the same time heat to the condenser, the latter quantity being related to the former by some hypothesis concerning the nature of heat. So in the reverse process by the performance of work heat may be drawn from the condenser and restored to the source.

Hence, if we employ the excess $W' - W$ of work furnished by the engines A and B, when working as already indicated, to drive another engine working in the reverse manner between the same source and refrigerator, this third engine will transfer heat from the colder body to the warmer—that is, on the whole, without the expenditure of any work the heat could be continually transferred from the colder to the warmer of two bodies. If this be admitted as impossible, the second fundamental principle may be stated in either of the following forms for a cyclic process.

Second law. "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature, or heat cannot of itself (that is, without compensation) pass from a colder to a warmer body" (Clausius).

The equivalent statement by Lord Kelvin is that "it is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects."

In making these statements it must be remembered that they apply only to the continued performance of useful work—that is, to engines working in complete cycles. Without this limitation, it might be objected, for example, that work could be derived from a highly compressed gas by simply allowing it to expand. During the expansion it would do work against external pressure, this work would be derived from the heat of the gas alone, no condenser being required, and the substance might be thus cooled much below the temperature of the surrounding bodies. If, however, a complete

cycle be performed, so that the substance is left in its initial condition, then the principle applies in either of the forms given above.[1]

288. Determination of the Efficiency.—The efficiency of a heat-engine has been defined as the ratio of the quantity of work performed to the quantity of heat drawn from the source, and in the case of a reversible engine we have seen that this efficiency is independent of the nature of the working substance. It must, therefore, be determined completely by the two temperatures between which it works. This is expressed by saying that the efficiency is some function of the temperatures of the source and condenser, or algebraically expressed

$$\frac{W}{Q}=f(\theta,\theta').$$

According to the dynamical theory W may be replaced by $Q-Q'$, the difference between the quantity of heat drawn from the source and that yielded to the condenser, and the expression for the efficiency becomes

$$\frac{Q-Q'}{Q}=f(\theta,\theta').$$

From this it follows that Q/Q' is a function of θ and θ', and therefore, if Q_1 and Q_2 be the quantities of heat taken in and ejected by a reversible engine working between the temperatures θ_1 and θ_2, we have

$$\frac{Q_1}{Q_2}=F(\theta_1,\theta_2),$$

when $F(\theta_1,\theta_2)$ is some function of θ_1 and θ_2.

Now returning to Carnot's cycle (Fig. 167), it is clear that Q_1, the quantity of heat absorbed along the isothermal DA, can depend only on the temperature θ_1, the nature of the working substance, and its pressure and volume in the initial and final states—that is, on the co-ordinates of D and A. Hence we may write

$$Q_1=f(\theta_1,N,p,v),$$

where N refers to the nature of the working substance. Similarly we have

$$Q_2=f(\theta_2,N,p,v).$$

Hence

$$\frac{Q_1}{Q_2}=\frac{f(\theta_1,N,p,v)}{f(\theta_2,N,p,v)},$$

and this must be independent of everything except θ_1 and θ_2, and

[1] Even though we could deal with the individual molecules, the second law in its broadest sense would not be violated, for work would still be obtained by using up the energy of the warmer molecules, and by transferring heat from the warmer to the colder.

consequently $f(\theta_1 N, p, v)$ must be of the form $Kf(\theta_1)$, where K involves everything depending on N, p, and v, so that we have [1]

$$\frac{Q_1}{Q_2}=\frac{Kf(\theta_1)}{Kf(\theta_2)}=\frac{f(\theta_1)}{f(\theta_2)}.$$

New scale. Now Q_1 is always greater than Q_2, hence $f(\theta_1)$ is always greater than $f(\theta_2)$ if θ_1 is greater than θ_2. The function $f(\theta)$ is consequently such that its magnitude increases as the temperature θ increases, and we might therefore form a new scale of temperature by tabulating the values of this function (if once determined) for all values of the centigrade measure θ. The values of this function might therefore be used to denote the corresponding temperatures on the new scale. So that if we denote $f(\theta)$ by τ we shall have

$$\frac{Q_1}{Q_2}=\frac{\tau_1}{\tau_2}, \quad \text{or } \frac{Q_1}{\tau_1}=\frac{Q_2}{\tau_2},$$

and the new scale of temperature will be such that any two temperatures on it bear to each other the same ratio as the quantities of heat taken in and ejected by a reversible engine working between these temperatures as source and condenser. The efficiency of such an engine will consequently be

$$\frac{Q_1-Q_2}{Q_1}=\frac{\tau_1-\tau_2}{\tau_1}.$$

289. Carnot's Function.—In the case of an engine working between two infinitely near temperatures, τ and $\tau+d\tau$ (or θ and $\theta+d\theta$), the efficiency is obviously

$$\eta=\frac{d\tau}{\tau} \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

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[1] This relation may also be established as follows:—We have, for an engine working between the limits θ_1 and θ_2,

$$\frac{Q_1}{Q_2}=F(\theta_1,\theta_2),$$

and, in the same manner for an engine working between the limits θ_2 and θ_3, we have

$$\frac{Q_2}{Q_3}=F(\theta_2,\theta_3).$$

Consequently by multiplication we find

$$\frac{Q_1}{Q_3}=F(\theta_1,\theta_2)F(\theta_2,\theta_3).$$

But Q_1/Q_3 must be equal to $F(\theta_1,\theta_3)$, therefore

$$F(\theta_1,\theta_3)=F(\theta_1,\theta_2)F(\theta_2,\theta_3);$$

that is, θ_2 must disappear from the right-hand member. In order that this may happen, the function F must be of the form

$$F(\theta_1,\theta_2)=\frac{f(\theta_1)}{f(\theta_2)},$$

and consequently we have

$$\frac{Q_1}{Q_2}=\frac{f(\theta_1)}{f(\theta_2)}.$$

Now in this case the efficiency must be some function of θ, since it depends only on θ and $\theta+d\theta$, and Carnot consequently wrote it in the form

$$\eta=\mu d\theta \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where μ is a function of θ to be determined, and is known as *Carnot's function.* Comparing (1) and (2) we find

$$\mu=\frac{1}{\tau}\frac{d\tau}{d\theta}=\frac{d}{d\theta}(\log\tau).$$

Hence if $d\tau/d\theta=1$, Carnot's function is numerically equal to the reciprocal of the absolute temperature. In general, with the foregoing notation, we have

$$\mu=\frac{f'(\theta)}{f(\theta)}.$$

290. Absolute Temperature and Absolute Zero.—The remarkable proposition established in the foregoing article was seized upon by Lord Kelvin[1] as early as 1848, and made the basis of a scale of absolute temperature—absolute in the sense of being independent of the properties of any particular substance.

We have seen that if Q_1 and Q_2 be the quantities of heat taken in and ejected by a reversible engine working between the limits of temperature θ_1 and θ_2, then the ratio Q_1/Q_2 is independent of the nature of the working substance, and depends only on the temperatures θ_1 and θ_2. Now the numbers expressing θ_1 and θ_2 will depend on the nature of the thermometric substance and on the system of thermometry adopted, and the ratio of θ_1 to θ_2 will depend in general on the system chosen; but, on the other hand, the quantities τ_1 and τ_2 are such that their ratio is independent of the nature of the working substance or of the system of thermometry adopted in the measurement of θ_1 and θ_2. If therefore the numbers expressing τ_1 and τ_2 are taken to represent the temperatures at which the heat is taken in and ejected by a reversible engine, we can assert that the ratio of any two temperatures on this scale is equal to the ratio of the quantities of heat taken in and ejected by a reversible engine working between these limits, and is independent of the properties of any particular substance.

This mode of reckoning temperature leads us to the notion of an absolute zero of temperature, for if the heat Q_2 ejected by an engine be zero, then τ_2 will be zero also, and the efficiency of the engine will be unity. All the heat Q_1 taken in from the source will be converted into work; and since we cannot suppose that more heat can be converted into work than that which is drawn from the source, it is impossible for τ to be negative, and hence the temperature corresponding to $\tau=0$ is the lowest possible temperature conceivable. The zero

[1] Wm. Thomson, *Proc. Cambridge Phil. Soc.*, or *Phil. Mag.*, 1848, and *Trans. Roy. Soc.*, Edin., 1854.

of this scale is consequently an absolute zero of temperature independent of the properties of any particular substance, for when the efficiency of one reversible engine is unity, the efficiency of every other reversible engine working between the same source and condenser will also be unity, and hence, if τ is zero for one substance, it will also be zero for every other. This zero is therefore absolute.

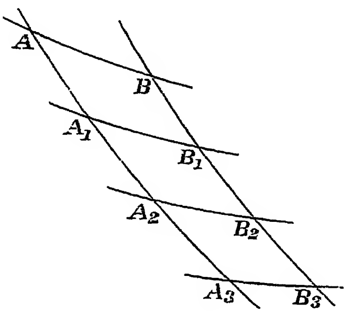

Fig. 168.

Lord Kelvin's system of reckoning temperatures is exhibited graphically as follows:—Let AA_1A_2 and BB_1B_2 (Fig. 168) be any pair of adiabatic lines for any substance chosen at random. These lines correspond to the state of the body before and after some arbitrary quantity of heat has been added to it. Let AB be any isothermal line for the same substance, and let A_1B_1, A_2B_2, etc., be other isothermals drawn, so that the areas of the cycles ABB_1A_1, $A_1B_1B_2A_2$, $A_2B_2B_3A_3$, etc., are equal to each other. In this case we have

$$Q - Q_1 = Q_1 - Q_2 = Q_2 - Q_3 = \text{etc.},$$

and hence, since $Q/\tau = Q_1/\tau_1$, we must have

$$\tau - \tau_1 = \tau_1 - \tau_2 = \tau_2 - \tau_3 = \text{etc.};$$

in other words, the isothermals have been drawn so as to correspond to equal differences of temperature, so that if $\tau - \tau_1$ be the unit of temperature, $\tau - \tau_2$ will be two units, $\tau - \tau_3$ three units, and so on. Lord Kelvin's method of graduating the scale of temperature is consequently equivalent to saying that the number of degrees between the temperature τ corresponding to the isothermal AB and the temperature τ' corresponding to any other isothermal A′B′ is to be taken proportional to the area ABB′A′.

The absolute zero of temperature being that which corresponds to $Q = 0$, the only thing which yet remains arbitrary is the size of the degree, and this may be chosen so that the number of degrees between two standard temperatures on our new scale is the same as that on one of the ordinary scales, for example, so that there may be 100 degrees between the freezing and boiling points of water. As soon as the number corresponding to one of these points has been determined, the numerical value of every other temperature is settled in a manner independent of the laws of expansion of any particular substance. To determine the number on the absolute scale which corresponds to

the freezing point or boiling point of water requires a special investigation of the behaviour of some particular substance. The simplest case is that of a perfect gas—that is, an ideal substance which obeys Boyle's law at all temperatures.

If the working substance be a perfect gas, the characteristic equation of which is Case of a perfect gas.

$$pv = R\Theta,$$

where Θ is the temperature measured from the zero of a thermometer filled with this substance, as indicated in Art. 82, then the quantity of heat Q taken in by the substance while passing from A to B along an isothermal is, in dynamical units,

$$Q = \int_{v_1}^{v_2} p dv = R\Theta \int_{v_1}^{v_2} \frac{dv}{v} = R\Theta \log \frac{v_2}{v_1},$$

and the quantity Q′ ejected in returning along A′B′, the lower isothermal Θ' of a Carnot's cycle is

$$Q' = \int_{v_4}^{v_3} p dv = R\Theta' \int_{v_4}^{v_3} \frac{dv}{v} = R\Theta' \log \frac{v_3}{v_4}.$$

Hence we have

$$\frac{Q}{Q'} = \frac{\Theta}{\Theta'} \frac{\log (v_2/v_1)}{\log (v_3/v_4)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

But since A and A′ are on the same adiabatic, we have

$$p_1 v_1^{\gamma} = p_4 v_4^{\gamma}, \quad \text{and similarly } p_2 v_2^{\gamma} = p_3 v_3^{\gamma},$$

and consequently

$$\frac{p_2 v_2^{\gamma}}{p_1 v_1^{\gamma}} = \frac{p_3 v_3^{\gamma}}{p_4 v_4^{\gamma}} \quad . \quad . \quad . \quad . \quad (2)$$

But $p_1 v_1 = p_2 v_2$, and $p_3 v_3 = p_4 v_4$ by the isothermal conditions, therefore (2) becomes

$$\frac{v_2}{v_1} = \frac{v_3}{v_4},$$

and equation (1) becomes

$$\frac{Q}{Q'} = \frac{\Theta}{\Theta'}.$$

But $Q/Q' = \tau/\tau'$ on the absolute scale, therefore we have finally

$$\frac{\tau}{\tau'} = \frac{\Theta}{\Theta'};$$

or, in other words, the absolute zero on Lord Kelvin's scale is the same as the zero of the perfect gas thermometer. Now the coefficient of expansion of a gas has been found to be $\frac{1}{273}$ on the centigrade scale, so that when the interval between the freezing and the boiling points of water is divided into 100 equal parts, the zero of the perfect

gas thermometer will be 273 degrees below the freezing point of water, and this is what is meant by saying that the absolute zero is $-273°$ C., or that on the absolute scale the freezing point of water is $273°$, and the boiling point $373°$.

As no ordinary gas rigorously obeys the laws of a perfect gas, the number 273 obtained by observation of the expansion of air requires correction in respect to the deviations of air from the supposed ideal condition, and these deviations can only be determined by special experiment. For this reason a special examination of the properties of air was made by Joule and Thomson by a method which we shall consider subsequently (Sec. IX.).

291. Remarks on the supposed Violations of the Second Law.— We shall now consider briefly some of the objections which have been raised against the second fundamental principle. This principle, as stated by Clausius, asserts the impossibility of transferring heat from a cold body to a hot body without at the same time some equivalent or compensating transformation taking place, such as the expenditure of work, or, what amounts to the same thing, the passage of heat from some other hot body to a cold one. As stated by Thomson, the law asserts that the manner in which work is performed by a heat-engine is by the passage of heat from a hot body to a cold one, and it must be remembered that these statements apply to cyclic processes which can be repeated over and over again so that the transference of heat or the performance of work can be kept up continuously.

An equivalent statement is that work cannot be obtained by using up the heat of a single body; or, in other words, we require two bodies at different temperatures, the obvious reason being that in order to obtain work continuously we require a working substance which alternately expands and contracts, and to produce this alternation of volume we require a corresponding alternation of temperature. For example, a gas may be enclosed under high pressure in a cylinder, and by allowing the gas to expand, work may be done while it cools below the temperature of any of the surrounding bodies, and it might appear that Thomson's statement was violated, but it must be remembered that this operation is not cyclic. It cannot be repeated without bringing the gas back again to its initial condition, and this would require either an expenditure of work or the passage of heat from some hot body to a cold one.

Two objections have been proposed by Hirn, and refuted by Clausius, and they are worthy of note as illustrations of the principle. In the first a horizontal cylinder (Fig. 169) is supposed fitted with a frictionless non-conducting piston which divides it into two com-

partments, A and B. These compartments are filled with air at temperatures θ_1 and θ_2 respectively. Now let us suppose that θ_1 is less than θ_2, and that the end of the compartment A is brought into thermal communication with a source of heat at a temperature greater than θ_1 but less than θ_2, then the pressure in A will increase, the piston will be pushed forward from A towards B so that the air in B is compressed, and as a consequence its temperature is raised. Thus heat leaves a body at a temperature less than θ_2, and enters a body at or above θ_2. It would appear at first sight that heat had passed from a cold body to a warm one, and that the axiom of Clausius was violated. What really happens, however, is that heat passes from a warm body to a cold one, and in addition there is also a transference of heat from a cold body to a hot one; this latter transference is consequently compensated by the former. The heat generated in B is the equivalent of the work done on it by the gas in A, and the power of doing this work is derived from the passage of heat into A from a body at a higher temperature.

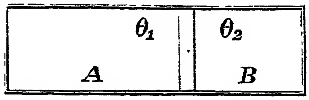

Fig. 169.

The second objection of Hirn is perhaps more ingenious than the first. Two non-conducting cylinders A and B (Fig. 170) of equal cross-section are fitted with frictionless pistons of equal weight, which are forced to move in opposite directions by a toothed wheel, so that when the wheel revolves one of them is drawn up while the other is forced down without any expenditure of work. By this arrangement the total volume of the spaces A and B enclosed between the pistons is kept constant. This space is filled with air, and at the beginning of the operation all the air is in the cylinder A, so that the piston in A is at the top of its stroke, while that in B is at the bottom.

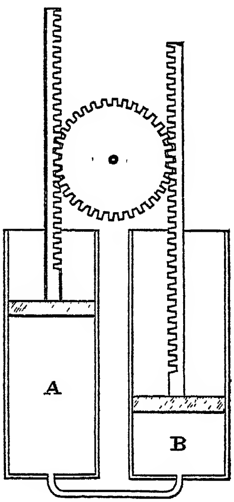

Fig. 170.

Let the temperature of the air in A be θ_0, and let the connecting tube be kept at some fixed temperature θ_1 higher than θ_0, while the wheel is slowly turned so that the air passes from A to B. The action which takes place will then be as follows:—The first instalment of air that enters B will be raised in temperature to θ_1, and in consequence the pressure will increase so that the air in A will be compressed and raised in temperature. The second instalment will also enter B at θ_1,

and the pressure will go on increasing as more air enters B, so that the air in B as well as that in A will be raised in temperature. The upper layers of air in B will therefore be raised to temperatures exceeding θ_1, and the average temperature of the mass in B will exceed that of the source of heat.[1] It would thus appear that heat has been transferred from a lower to a higher temperature without the expenditure of work. But it appears at once in this case, as in the previous, that there is also a compensating process in operation, for while the air is passing through the connecting tube it is heated to θ_1, and there is thus a transference of heat from a higher to a lower temperature.

In both cases consequently there are two processes in operation: one a transference of heat from a higher to a lower temperature, and the other from a lower to a higher. There are thus really two engines at work in all these cases, one working in the direct cycle and driving the other backwards in the reversed cycle.

A somewhat similar process is stated by M. Bertrand.[2] Here a gas at θ is enclosed in a cylinder fitted with a movable piston, and the end of the cylinder is in thermal communication with a source of heat at θ. The gas is allowed to expand, doing external work, while its temperature is kept constantly at θ, and this work is stored up and subsequently employed to compress the gas, thereby raising its temperature so that it may yield heat to a body at a temperature higher than θ. The compensating process is, however, in operation in this case also, for during the expansion of the gas its temperature must be somewhat below θ, and the heat which it gains from the source passes from a higher to a lower temperature.

The second law is also practically embodied in the statement that it is impossible to produce any difference of temperature or pressure in an isolated mass at uniform temperature and pressure throughout without the expenditure of work, and to the statement in this form Maxwell[3] has devised an ingenious but illusory violation. He takes the case of a mass of gas at uniform temperature and pressure throughout, and he then imagines a being capable of dealing with the individual molecules of the gas. According to the ordinary theory these molecules are moving with velocities which differ considerably, so that if a partition be supposed erected in the enclosure, the imaginary being may sift the molecules so as to accumulate the faster-moving molecules in one region and the slower molecules in the other. By

[1] If the air in A be initially at 0° C., and if the connecting tube be kept at 100° C., the average temperature of the whole mass when transferred to B will be about 120° C.

[2] Bertrand, *Thermodynamique*, p. 85.

[3] *Theory of Heat*, 3rd edition, p. 328.

this means inequalities of temperature and pressure might be introduced without the expenditure of any work.

It must be remembered, however, that to this being the gas is by no means a uniformly heated mass. The faster-moving molecules are hot and the slower cold, and the whole mass to him is made up of discrete parts at very different temperatures, and this sifting of the molecules is no more a violation of the second law than would be the collection by an ordinary being of the warmer members of a system of bodies into one region of space and the colder into another.

The individual molecules become *bodies* when we are able to deal with them, and in Maxwell's case there is no transference of heat from a cold molecule to a hot one, there is only a sifting of hot from cold, and if work were to be obtained it would be by the passage of heat from a hot one to a cold one. When we are furnished with a system of bodies moving with different velocities work may be obtained from the members of the system as long as any relative motion remains, but it will always be obtained at the expense of the faster-moving members, or, as we may say, from the warmer members of the system. Thus Maxwell's demon might use up the energy of the faster-moving molecules until they all came to relative rest, but throughout the operation the transference of energy will always be from bodies of higher to bodies of lower temperature.

The point then appears to be that a clear understanding of the meaning of the word *body* should be obtained in stating the second law, for, without this, supposed violations can be easily manufactured by a confusion of terms.

Examples

1. Prove that an adiabatic curve cannot intersect an isothermal in more than one point, and therefore cannot touch it.

[If an adiabatic and an isothermal intersected in two points, they would form a closed cycle, and work could be performed with a single source at the temperature of the isothermal.]

2. In passing along an adiabatic, prove that the temperature must always change in the same sense.

[Otherwise the same temperature would exist at two or more points on the same adiabatic.]

3. In the same manner the quantity dQ must always have the same sign in passing along an isothermal.

4. Of all the cycles that a mass of gas can pass through between given extreme temperatures, the cycle of Carnot gives the maximum ratio of the work performed to the heat spent.

5. If an isothermal and an adiabatic intersect at a point M (Fig. 171), making angles A, B, C, D, show that in passing to any other state M′—

(1) If M′ lies in A there is heating accompanied by a subtraction of heat.

(2) If M′ lies in B there is heating accompanied by a communication of heat.

(3) If M′ lies in C there is cooling accompanied by a communication of heat.

(4) If M′ lies in D there is cooling accompanied by a subtraction of heat.

6. In general, if two adiabatic tangents be drawn at A and A′ (Fig. 172), and

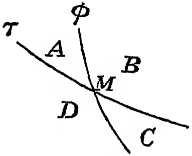

Fig 171.

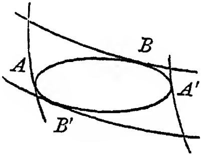

Fig. 172.

two isothermal tangents at B and B′ to any closed cycle, there will be a communication of heat in passing along ABA′, and a subtraction of heat in passing back along A′B′A, while there will be a fall of temperature in passing along BA′B′ and a rise of temperature in passing along B′AB.

SECTION IV

ON ENTROPY AND AVAILABLE ENERGY

292. Extension of Carnot's Cycle—The Theorem of Clausius.—In the case of a simple Carnot's cycle the quantities of heat taken in and ejected during the isothermal transformations at absolute temperatures τ_1 and τ_2 are connected with these temperatures by the equation

$$\frac{Q_1}{\tau_1}=\frac{Q_2}{\tau_2};$$

or, if quantities of heat taken in be regarded as positive, while quantities given out are considered negative, this relation may be written in the form

$$\frac{Q_1}{\tau_1}+\frac{Q_2}{\tau_2}=0.$$

Now in the case of a general transformation, represented graphically by a curve of any form, the heat is not all taken in at the same temperature and given out at another, but is taken in and given out

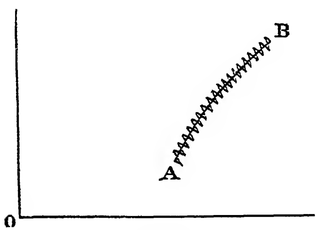

Fig. 173.

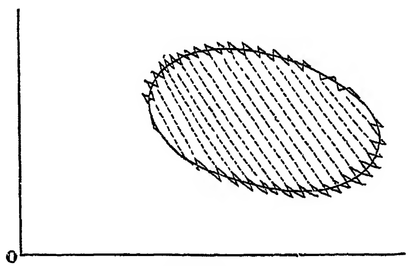

Fig. 174.

at temperatures which vary continuously. The above relation may, however, be extended to any reversible transformation by the following simple method suggested by Clausius :—[1]

Let the curve AB (Fig. 173) represent any reversible transforma-

[1] Clausius, *Mechanical Theory of Heat*, p. 88.

tion whatever, which brings the working substance from the state A to the state B. This whole transformation may be considered as made up of an immense number of very small transformations, which are alternately isothermal and adiabatic, as shown by the zigzag line overrunning AB, the successive elements of which are alternately elements of isothermal and adiabatic curves. The smaller the elements of this zigzag line, the more closely will it coincide with the continuous curve AB, and the coincidence will be indefinitely close when the elements are taken indefinitely small. Hence, if the continuous transformation AB is replaced by the zigzag of alternate isothermals and adiabatics, the effect on the quantities of heat, and the corresponding temperatures at which they are taken in or ejected, will be vanishingly small.

From these considerations it follows that any reversible cycle represented by any closed curve may be broken up into an infinite number of indefinitely small Carnot cycles, as shown in Fig. 174. For each of these cycles we have, if dQ_1 be the quantity of heat absorbed at τ_1 and $-dQ_2$ the quantity ejected at τ_2—

$$\frac{dQ_1}{\tau_1}+\frac{dQ_2}{\tau_2}=0\,;$$

and by taking the sum of these for all the cycles, we have for any cyclic reversible transformation whatever

$$\int\frac{dQ}{\tau}=0.$$

In Carnot's cycle the working substance is supposed to take in heat at the temperature of the hot body, and eject it at the temperature of the cold body. In practice, however, the working substance must be somewhat colder than the source when taking in heat, and warmer than the refrigerator when giving it out. Hence, if ABCD (Fig. 175) be the cycle of Carnot in the ideal limit, the practical cycle will be represented by the dotted figure[1] A′B′C′D′. The area of the latter will be less than that of the former, so that the efficiency in practice will be less than that of the ideal case. Consequently, if Q_1 and Q_2 are the quantities of heat taken in and ejected,

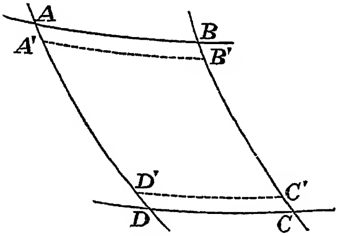

Fig. 175.

[1] When the operation is reversed, A′B′ will be above AB, and C′D′ below CD, and the area of the reverse cycle will exceed that of the direct.

and τ_1 and τ_2 the absolute temperatures of the source and refrigerator, we have

$$\frac{Q_1 - Q_2}{Q_1} < \frac{\tau_1 - \tau_2}{\tau_1},$$

which gives at once $Q_1/\tau_1 < Q_2/\tau_2$, or

$$\frac{Q_1}{\tau_1} - \frac{Q_2}{\tau_2} < 0.$$

If, however, τ_1 and τ_2 denote the absolute temperatures of the working substance when taking in and giving out heat, we have still

$$\frac{Q_1}{\tau_1} - \frac{Q_2}{\tau_2} = 0;$$

and that the left-hand member is less than zero when τ_1 and τ_2 denote the absolute temperatures of the hot and cold bodies, follows at once from the fact that in this case the temperature of the source is higher than that of the working substance, while that of the condenser is lower; and, as a consequence, Q_1/τ_1 is diminished, while Q_2/τ_2 is increased.

In the same manner, if in any closed cycle the working substance be not at the same temperature as the body from which it absorbs, or to which it ejects heat, then we have

$$\int \frac{dQ}{\tau} = 0,$$

when the temperature τ is that of the working substance when it takes in or ejects the quantity of heat dQ;[1] but if τ be the temperature of the body to which the working substance yields heat or from which it abstracts it, then the positive constituents of this integral are all diminished, while the negative are increased, and we have

$$\int \frac{dQ}{\tau} < 0.$$

293. Entropy.—The interpretation of the theorem of the preceding article is that the value of the integral for any reversible transformation which brings a body from a condition represented by any point A to that represented by any other point B, depends only on the initial and final conditions, or is a function of the co-ordinates of A and B. For if ϕ be the value of the integral taken along any path AMB (Fig. 166), and ϕ' its value when the transformation is effected along any other path ANB joining the same pair of points, then the pair of paths AMB and ANB form a closed reversible cycle, and for

[1] dQ is the whole quantity of heat gained either from external or internal agencies.

the whole cycle the value of the integral must vanish; therefore $\phi - \phi' = 0$, or $\phi = \phi'$. The meaning of this is that the value of ϕ at any point depends only on the co-ordinates of the point, or that dQ/τ is a perfect differential—that is, the complete differential of some function ϕ, so that

$$\frac{dQ}{\tau} = d\phi,$$

and the value of the integral taken along any path joining the points whose co-ordinates are p_1v_1 and p_2v_2 is

$$\int_2^1 \frac{dQ}{\tau} = \phi_1 - \phi_2,$$

where ϕ_1 is the value of the function ϕ at the point p_1v_1, and ϕ_2 its value at p_2v_2.

By working along an isothermal line τ remains constant, and the value of ϕ changes by an amount Q/τ, where Q is the quantity of heat added to or taken from the substance during the transformation. This suggests the measurement of ϕ from a zero at which the substance contains no heat, but in practice it is with the changes of ϕ rather than with its absolute value that we are mainly concerned, so that we may measure ϕ (as we measure potential in dynamics) from any assumed origin; and the value of the integral taken along any path drawn from this origin to any other point may be written in the form

$$\int \frac{dQ}{\tau} = \phi.$$

The function ϕ has been termed the *entropy* of the substance by Clausius;[1] and it is clear that throughout any adiabatic transformation the entropy of a body at the same temperature throughout remains constant; for if $dQ = 0$, we have $d\phi = 0$, and this means that ϕ remains constant. The adiabatic lines of any substance are consequently lines of constant entropy, and for this reason they have been also named *isentropics.* If, however, any body be subject to operations which produce inequalities of temperature in the mass, there will be a transference of heat from the warmer to the colder parts by conduction and radiation, and although the body may neither receive heat from nor give it out to other bodies (so that the transformation is adiabatic-

[1] R. Clausius (*Pogg. Ann.*, vol. cxxv. p. 390) introduced the idea of a transformation equivalent of a quantity of heat, and dQ/τ is the transformation equivalent of the quantity dQ. The name entropy was consequently chosen from the Greek word τροπή, signifying transformation.

throughout), yet on account of the inequalities of temperature, the entropy of the mass will increase as explained below (p. 629), and under these circumstances the transformation will not be isentropic.

It has been already pointed out (Art. 283) that the quantity of heat absorbed or given out by a body in passing from one condition to another is not determined completely by the initial and final conditions, that Q is not expressible in terms of the initial and final co-ordinates, or that dQ is not a perfect differential. But we have just seen that dQ/τ is a perfect differential, and this means that τ is the integrating divisor of dQ, or $1/\tau$ is its integrating factor.

294. Clausius's Theorem considered as the Second Law.—The theorem of Clausius that in any closed reversible cycle we have

$$\int\frac{dQ}{\tau}=0 \qquad (1)$$

or, in other words, that the change of entropy of a system subject to any reversible transformation depends only on the initial and final conditions of the system, has been deduced merely as a generalisation of the equation

$$\frac{Q_1}{\tau_1}+\frac{Q_2}{\tau_2}=0 \qquad (2)$$

which applies to a simple Carnot's cycle. This latter equation depends on the theorem of Carnot that the efficiency of a reversible engine depends only on the temperatures of the source and refrigerator; and in deducing this theorem from the point of view of the dynamical theory, the only principle made use of is the second law in any one of the forms stated in Art. 287. It follows, therefore, that equation (1) is only a mathematical representation of the second law, and it has consequently been customary with many writers to write down equation (1) as the second law of thermodynamics. We have avoided this because it appears preferable to state the main axiom in its primitive form as the second law rather than any mathematical disguise of it, for the fundamental postulate is by this means kept more prominently in view.

Since equation (1) contains the second law, it ought to be possible to deduce this law from it. Thus, starting with (1)—that is, that the entropy of a body is the same at the end as at the beginning of any closed reversible cycle of operations—let us suppose that the body has returned to its initial condition, so that the entropy has now attained its initial value. Now, if any exchange of heat has taken place during the cycle between the working substance and other bodies, for example, if dQ_1 has been taken in by the working substance

at τ_1, and if dQ_2 has been given out at τ_2, then, in order that the entropy may remain unaltered, this exchange must take place in such a way that

$$\frac{dQ_1}{\tau_1}=\frac{dQ_2}{\tau_2}.$$

Hence if τ_2 is less than τ_1, it follows that dQ_2 is less than dQ_1, or the quantity of heat gained by the cold body is less than that lost by the hot body, so that work is done during the cycle by drawing heat from the warmer of two bodies and giving it in part to the colder.

295. Entropy of a System.—The entropy of a body being taken arbitrarily as zero in some standard condition A (Fig. 176), defined by some standard temperature and pressure (or volume), the entropy in any other state B is the value of $\int\frac{dQ}{\tau}$ taken along any reversible path by which the body may be brought to B from the standard state A. The path may obviously be an arc AC (Fig. 176) of an isothermal line passing through the point defining the standard state, together with the arc BC of the adiabatic line passing through B. The entropy in the state B may consequently be measured thus. ~~Let the~~ volume be changed adiabatically until the standard temperature τ is attained, and then change the volume isothermally until the standard pressure is attained. If the quantity of heat imparted during the latter operation be Q, the entropy in the state B is

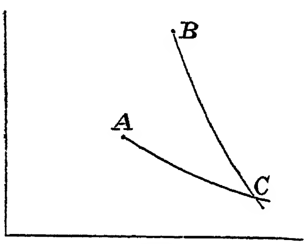

Fig. 176.

$$\phi=\frac{Q}{\tau}.$$

In this operation the temperature and pressure are supposed uniform throughout the body; and if the mass in this case be unity, it is clear that the quantity of heat imparted when the mass is m will be mQ, so that the entropy of a mass m in the state B will be $m\phi$ where ϕ is the entropy per unit mass. This amounts to saying that the entropy of two units of mass in a given condition is twice that of one unit.

Hence, if we have a system of bodies at different temperatures τ_1, τ_2, etc., and masses m_1, m_2, etc., the entropy of the system will be the sum of the entropies of its parts or

$$\Phi=m_1\phi_1+m_2\phi_2+m_3\phi_3+\ .\ .\ .\ \text{etc.}=\Sigma(m\phi),$$

where ϕ_1, ϕ_2, etc., are the entropies per unit mass of m_1, m_2, etc. The

average entropy of the system per unit mass might therefore be defined as

$$\frac{\Phi}{\Sigma(m)} = \frac{\Sigma(m\phi)}{\Sigma(m)},$$

just as the whole volume of a system is $V = \Sigma(mv)$, and the average volume per unit mass may be taken as $\Sigma(mv)/\Sigma(m)$.

296. Increase of Entropy caused by Equalisation of Temperature.—All processes, such as radiation, convection, and conduction, by which the temperatures of the various parts of a system become equalised, change the entropy of the system, and it is easily shown that the result of such operations is to increase the entropy. For if a quantity of heat dQ leaves a body at temperature τ_1, the entropy of this body will be diminished by an amount $d\phi_1 = dQ/\tau_1$, and if this same quantity passes into a body at a lower temperature τ_2, its increase of entropy will be $d\phi_2 = dQ/\tau_2$. Consequently the increase of entropy of the pair will be

$$d\phi_2 - d\phi_1 = dQ\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right);$$

and this is a positive quantity, since τ_2 is less than τ_1.

Since such processes as radiation and conduction tend to reduce, rather than to exaggerate, differences of temperature, it follows that the entropy of the material universe, as we know it, must be continually increasing—that is, the entropy of the universe is growing towards a maximum value which will be attained when all temperature difference ceases to exist.

297. Available Energy or Motivity.—When an engine working between any source and refrigerator draws a quantity of heat Q from the source, we have seen that the whole of this quantity is not converted into work but only a fraction of it—viz. ηQ, where η is the efficiency of the engine. The remainder is given to the refrigerator; and if the refrigerator is the coldest body of the system, this quantity remains unavailable for the purposes of work. If τ_0 be the temperature of the coldest body of a system, and if this body be used as the refrigerator of an engine describing Carnot's cycle, then when a quantity dQ of heat is drawn from a source at temperature τ, the fraction of this which can be converted into work is

$$\frac{\tau - \tau_0}{\tau} dQ.$$

This available fraction of dQ has been termed its *motivity* by Lord Kelvin;[1] and it follows that a quantity of heat is wholly available for conversion into work only when the refrigerator is at the

[1] W. Thomson, *Phil. Mag.*, and *Proc. Roy. Soc.*, Edin., 1852.

absolute zero of temperature, and in this case the motivity of a quantity of heat is equal to the whole quantity.

The motivity of any quantity is simply its practical value, and it is only when the refrigerator is at absolute zero that the motivity becomes equal to the dynamical value dQ.

298. Dissipation of Energy.—If τ_0 be the temperature of the coldest body of a system, the motivity of a quantity of heat dQ at temperature τ is

$$\left(1-\frac{\tau_0}{\tau}\right)dQ.$$

If the quantity dQ be taken in by an engine describing Carnot's cycle, and if the quantity dQ' be ejected at the temperature τ' by the same engine, the motivity still remaining in dQ' is

$$\left(1-\frac{\tau_0}{\tau'}\right)dQ',$$

so that the change of motivity of the system is

$$dQ-dQ'-\tau_0\left(\frac{dQ}{\tau}-\frac{dQ'}{\tau'}\right);$$

and consequently if the working substance describes ~~any closed~~ cycle, the change of motivity is

$$Q-Q'-\tau_0\int\frac{dQ}{\tau},$$

where Q is the whole quantity of heat taken in and Q′ the whole quantity given out by the working substance during the cycle. If the cycle be reversible, the loss of motivity will be simply $Q-Q'$, so that for a reversible cycle the integral vanishes; but if the cycle be not reversible, the loss of motivity will be greater than $Q-Q'$, and consequently the integral taken round such a cycle must have a negative value. There is thus a waste of motivity or a dissipation of energy of the positive value

$$D=-\tau_0\int\frac{dQ}{\tau}.$$

If a quantity of heat Q passes from a body at temperature τ_1 to another at a lower temperature τ_2, the loss of availability is

$$\tau_0 Q\left(\frac{1}{\tau_2}-\frac{1}{\tau_1}\right)—$$

that is, the loss of availability or the dissipation is measured by the product of τ_0 and the increase of entropy.

As has been already pointed out, the efficiency of every engine falls short of the ideal limit of the reversible engine, so in practice

when it is attempted to transform energy, a part of it is necessarily dissipated. Further, as the energy of the universe is constantly undergoing transformation, there is a constant dissipation in operation, and a constant degradation to the final unavailable state of uniformly diffused heat. The statement, therefore, that the entropy of the universe is tending towards a maximum, amounts to saying that the available energy of the universe is tending towards zero.

299. Graphic Representations.—The condition of a substance being determined by the co-ordinates of any point A (Fig. 177), we may speak of the whole energy of the substance in this state, although this is a quantity which we have no means of ascertaining experimentally. We cannot deprive a body of all its heat, and in the case of bodies which assume the gaseous condition, we cannot allow the volume of the containing vessel to increase sufficiently to obtain all the work derivable from the expansion of the substance, and so we cannot determine the whole energy. Nevertheless, when a body passes from any state A to any other B, by means of any transformation represented graphically by the curve AB, we can determine how much energy the body receives or loses, and in practice this is all we want.

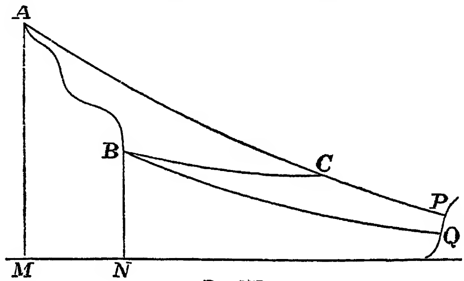

Fig. 177.

Thus, if AP and BQ represent the adiabatic curves passing through A and B, and if PQ be a fictitious curve representing the zero isothermal, then the area APQB (Art. 69) is the equivalent of the heat lost by the body in passing from A to B (when B is below the line AP the heat will be lost). So, also, the area ABNM represents the external work done by the body during the transformation (when B is to the right of A the body expands and does external work). Hence, in passing from A to B the whole energy lost by the body will be represented by the area APQBNM, and this area is independent of the form of the curve AB. It is to be noted, on the other hand, that the area ABNM and the area APQB both depend on the shape of the curve, and consequently, although the external work done and the quantity of heat emitted both depend on the nature of the transformation, the change of energy of the substance is completely determined by the co-ordinates of the initial and final states (cf. Art. 283).

Hence,

$$\text{Area APQBNM} = \text{U} - \text{U}_0 = \text{change of energy.}$$
$$\text{Area ABMN} = \text{W} = \int p dv.$$
$$\text{Area APQB} = \text{Q} = \int \tau d\phi.$$

If the temperature corresponding to B—that is, the temperature τ_0 of the isothermal BC—be the lowest available temperature (for example, if the body be surrounded by a medium at this temperature), then in passing from A to B the temperature of the body cannot fall below τ_0, and no part of the curve AB can descend below BC, and since the body receives no heat from outside, the curve AB cannot rise above AP. The supposed conditions consequently constrain the path AB to lie within a certain region, and under these conditions it is clear that when it coincides with the limiting path ACB, made up of the arc AC of an adiabatic and the arc BC of the isothermal through B, the quantity of heat lost will be least and the quantity of external work done by the body will be greatest. The path ACB is consequently the path of least loss of heat, and the area ACBNM represents the maximum amount of work that can be derived by bringing the substance from A to B under the supposed conditions. This area, therefore, represents the whole energy available for transformation into work. The quantity of heat given out along this path is obviously

Path of least heat.

$$\text{Q} = \tau_0(\phi - \phi_0) = \text{area CPQB}$$

where ϕ_0 is the entropy in the state B and ϕ the entropy in the state A. It appears, therefore, that if U and U_0 be the whole energies in the states A and B respectively, then the work done during the transformation cannot exceed the area ACBNM, or

$$\text{U} - \text{U}_0 - \tau_0(\phi - \phi_0).$$

This, then, is the energy available for mechanical purposes under the circumstances, and it follows that the greater the original entropy of the body the less the available energy (see further, Sec. VIII.).

300. Work obtainable from an Unequally Heated Body.—In the case of a body whose parts are at different temperatures equalisation of temperature will be effected by radiation and conduction, and a corresponding dissipation of available energy will occur. When such a body is enclosed in a non-conducting envelope so as to be cut off from thermal communication with all other bodies, it becomes a definite problem to determine the amount of work that can be obtained by bringing all its parts to a common temperature by means of perfect thermodynamic engines working between them. The amount of work obtainable in this way has been investigated by Lord Kelvin,[1] and

[1] W. Thomson, *Phil. Mag.*, February 1853.

his results have been derived by Professor Tait[1] in the following simple manner:—

Let τ_0 be the final temperature of the body when brought to a uniform temperature by perfect engines, so that all the heat which disappears is converted into work. Then if another body at this temperature be used as a source or condenser for the engines according as they work between it and a part of the body colder or warmer than τ_0, this supplementary body must, on the whole, neither receive nor lose heat. Now, if an element of mass dm, of specific heat s and temperature τ, be brought to τ_0 by means of a perfect thermodynamic engine, it loses or gains a quantity of heat $\int_{\tau_0}^{\tau} sdmd\tau$, and the fraction of this, which is converted into work, is

$$dm\int_{\tau_0}^{\tau}\frac{\tau-\tau_0}{\tau}sd\tau.$$

The whole work done during the process is consequently

$$W=\int dm\int_{\tau_0}^{\tau}(\tau-\tau_0)s\frac{d\tau}{\tau} \qquad . \qquad . \qquad (1)$$

where s is measured in dynamical units.

Now the total quantity of heat taken in by an engine from the element dm is $\int_{\tau_0}^{\tau} sdmd\tau$, and consequently the quantity given out by this engine to the condenser at τ_0 is

$$dm\int_{\tau_0}^{\tau}\frac{\tau_0}{\tau}sd\tau.$$

Hence, since the condenser on the whole neither gains nor loses heat, we must have for the whole body

$$\int dm\int_{\tau_0}^{\tau}\frac{\tau_0}{\tau}sd\tau=0 \qquad . \qquad . \qquad . \qquad (2)$$

The equation (1) therefore becomes

$$W=\int dm\int_{\tau_0}^{\tau}sd\tau \qquad . \qquad . \qquad . \qquad (3)$$

This expression is much simplified by the supposition that the

[1] P. G. Tait, *Sketch of Thermodynamics*, p. 123.

specific heat s is independent of the temperature. In this case we have at once

$$W=\int(\tau-\tau_0)sdm \quad . \quad (4)$$

whereas equation (2) becomes

$$\int \log\left(\frac{\tau}{\tau_0}\right)sdm=0,$$

or

$$\log \tau_0=\frac{\int(\log \tau)sdm}{\int sdm} \quad . \quad . \quad . \quad (5)$$

If the body is homogeneous this expression simplifies still further, for then s is the same for all the elements, and if we write w_1 for the water equivalent of all the matter at the same temperature τ_1, we have $w_1=\int sdm$ (the summation extending to all the elements at temperature τ_1), and (4) becomes

$$W=s[\Sigma(w\tau)-\tau_0\Sigma(w)] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

while (5) takes the form

$$\log \tau_0=\frac{\Sigma w \log \tau}{\Sigma w}=\frac{\Sigma \log \tau^w}{\Sigma w}=\log\left(\tau_1^{w_1}\tau_2^{w_2}\tau_3^{w_3}\ldots\right)^{\frac{1}{\Sigma w}}.$$

Hence

$$\tau_0=\left(\tau_1^{w_1}\tau_2^{w_2}\tau_3^{w_3}\ldots\right)^{\frac{1}{\Sigma(w)}} \quad . \quad (7)$$

Cor. In the case of two equal masses at temperatures τ_1 and τ_2 respectively, we have

$$\tau_0=\sqrt{\tau_1\tau_2}$$

and

$$W=sm(\tau_1+\tau_2-2\sqrt{\tau_1\tau_2})=w(\sqrt{\tau_1}-\sqrt{\tau_2})^2,$$

both of which may be very simply deduced directly.

Examples

1. If a system of bodies at different temperatures and pressures be contained within an adiabatic enclosure of constant volume, prove that the quantity of energy converted into work will be greatest when the system is reduced to thermal and mechanical equilibrium as follows :—

(α) Change the volume of each body adiabatically till they all attain the same temperature.

(β) The bodies being all at the same temperature, let those under higher pressure expand isothermally and compress those under lower pressure until the pressures of all are equal.

[The entropy of the system remains the same throughout this process, since there is no communication of heat except between bodies at sensibly the same temperature, and the work gained is consequently greatest.]

2. In a Carnot's cycle bounded by two isothermals τ_1 and τ_2, and two isentropics ϕ_1 and ϕ_2, prove that the area is

$$(\tau_1-\tau_2)(\phi_1-\phi_2).$$

[We have $Q_1=\tau_1(\phi_1-\phi_2)$ and $Q_2=\tau_2(\phi_1-\phi_2)$, and the area is Q_1-Q_2 .·., etc.]

3. The area of a Carnot's cycle, bounded by two infinitely close isothermals and two infinitely close isentropics, is

$$d\tau d\phi.$$

4. A series of isothermals corresponding to absolute temperatures in arithmetical progression, and a similar arithmetic series of isentropics, form a network, the meshes of which are of equal area.

5. If the absolute temperature and the entropy be taken as co-ordinates to represent the state of a working substance, the area of any cycle represents the heat absorbed, or ejected.

[This follows from the relation $dQ=\tau d\phi$.]

6. The whole area between two isentropics and an isothermal is

$$\tau(\phi_1-\phi_2).$$

7. In the case of a perfect gas, determine the entropy and prove directly that for a closed cycle

$$\int\frac{dQ}{\tau}=0.$$

[In the case of a perfect gas we have (Art. 144)

$$\frac{dQ}{\tau}=C_v\frac{d\tau}{\tau}+R\frac{dv}{v},$$

$$\therefore\quad \phi_1-\phi_2=C_v\log\frac{\tau_1}{\tau_2}+R\log\frac{v_1}{v_2}=C_v\log\frac{p_1}{p_2}+C_p\log\frac{v_1}{v_2}.\Big]$$

8. Assuming the specific heat s of a liquid to be constant, determine the entropy per unit mass.

[Here $dQ=sd\tau$, .·. $\phi_1-\phi_2=s\log(\tau_1/\tau_2)$.]

9. A unit mass of liquid at τ is converted into saturated vapour at the same temperature; determine the change of entropy.

[Here we have

$$\phi_1-\phi_2=\int\frac{L dm}{\tau}=\frac{L}{\tau}.$$

Hence, if a unit mass of liquid at τ_0 be raised to τ and vaporised at this temperature, the change of entropy is

$$s\log\frac{\tau}{\tau_0}+\frac{L}{\tau},$$

and if in addition the vapour be superheated to a temperature τ', the change of entropy will be, assuming the superheated vapour to obey the laws of gases,

$$s\log\frac{\tau}{\tau_0}+\frac{L}{\tau}+C_v\log\frac{\tau'}{\tau}+R\log\frac{v'}{v}.$$

The entropy, like the internal energy, depends only on the initial and final conditions, and consequently the foregoing expression should be independent of the temperature τ of ebullition, so that

$$(s-C_v)\log\tau+L/\tau-R\log v=0.]$$

10. If a body describes a closed isothermal and if it is reversible its area is zero, consequently it consists of two or more loops (cf. p. 397).

11. If the internal energy of a body be a function of the temperature only, prove that its characteristic equation is of the form

$$p=\tau f(v).$$

[In this case we have $dQ=\frac{dU}{d\tau}d\tau+pdv$, therefore $d\phi=\frac{1}{\tau}\frac{dU}{d\tau}d\tau+\frac{p}{\tau}dv$, and consequently $\frac{p}{\tau}dv$ must be a perfect differential—that is, p/τ must be a function of v.]

12. If a substance be such that U increases uniformly with τ when v is constant, and uniformly with v when τ is constant, and if C_p be constant, find the characteristic equation.

[Evidently we must have $dU=ad\tau+bdv$, where a and b are constants. Therefore

$$dQ=\tau d\phi=dU+pdv=ad\tau+(b+p)dv \quad . \quad . \quad (1)$$

But since $d\phi$ is a perfect differential it follows that $(b+p)/\tau$ must be a function of v, or

$$b+p=\tau f(v) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence if p and τ be taken as independent variables, we have by (1) and (2)

$$dQ=\left[a+(b+p)\frac{dv}{d\tau}\right]d\tau+(b+p)\frac{dv}{dp}dp=\left(a-\frac{f^2}{f'}\right)d\tau+\frac{f}{f'}dp.$$

Therefore

$$C_p=\left(\frac{dQ}{d\tau}\right)_p=a-\frac{f^2}{f'}.$$

Hence

$$(a-C_p)\frac{df}{f^2}=dv, \quad \text{or } (C_p-a)=(v+c)f,$$

where c is a constant. But $f=(b+p)/\tau$, therefore the required relation is

$$(p+b)(v+c)=(C_p-a)\tau.]$$

13. If C_p and C_v be both constant, show that U may be expressed as a linear function of τ and v.

14. Two non-conducting vessels of volumes v_1 and v_2 are connected by a tube furnished with a tap. The vessels are filled with gas at the same temperature and at pressures p_1 and p_2 respectively. The tap is opened and the gas is allowed to fill both vessels; find the change of entropy, prove that it is positive, and explain why there is any change of entropy (cf. Art. 293).

15. If a substance obeys Boyle's law, and if its internal energy be a function of the temperature only, prove that its characteristic equation is

$$pv=R\tau$$

where R is a constant.

[If the substance obeys Boyle's law, then the function $f(v)$ of Ex. 11 must be simply a constant divided by v. Therefore, etc.]

16. If the characteristic equation of a substance be $pv=R\tau$, prove that the internal energy depends on the temperature only.

[We have

$$d\phi=\frac{dU}{\tau}+\frac{pdv}{\tau}=\frac{dU}{\tau}+R\frac{dv}{v}.$$

The final term being a perfect differential, it follows that dU/τ is a perfect differential, but dU is also a perfect differential, $\therefore$ etc.]

17. A unit mass of gas expands from a volume v_1 to a volume v_2 without doing external work (*e.g.* into an empty vessel); find the loss of motivity.

[*Ans.* $\tau_0 R \log (v_2/v_1)$.

SECTION V

THERMODYNAMIC FORMULÆ

301. Fundamental Differential Equations.—In general, the condition of a substance is completely determined by any pair of the quantities p, v, τ, ϕ, U, and in solving any thermodynamic problem, the pair most suitable for the purpose in hand must be chosen as independent variables. The quantities among which relations are most commonly established by the theory of heat are p, v, τ, ϕ, the two specific heats, and the latent heats of change of state. These variables are connected by two distinct equations

$$dQ = dU + dW \quad . \quad . \quad . \quad . \quad (1)$$

and

$$dQ = \tau d\phi \quad . \quad . \quad . \quad (2)$$

furnished by the first and second fundamental principles of thermodynamics. When two distinct equations are obtained between any number of variables, we can proceed by known methods to deduce other relations among the variables which are often very useful and remarkable.

Thus, starting from equations (1) and (2), we obtain by equating their right-hand members

$$\tau d\phi = dU + dW \quad . \quad (3)$$

or, in the case in which the only external force is a uniform normal pressure p, we have

$$dU = \tau d\phi - p dv \quad . \quad . \quad . \quad . \quad (4)$$

We shall deal at present with this simpler case, and proceed to express (4) in terms of any two independent variables x and y which determine the condition of the body. These symbols may be subsequently replaced by any pair of the quantities p, v, τ, ϕ at pleasure. Now since ϕ and v are supposed to be expressible in terms of x and y, we have

$$d\phi = \frac{d\phi}{dx}dx + \frac{d\phi}{dy}dy, \quad \text{and } dv = \frac{dv}{dx}dx + \frac{dv}{dy}dy.$$

Therefore equation (4) becomes

$$dU=\left(\tau\frac{d\phi}{dx}-p\frac{dv}{dx}\right)dx+\left(\tau\frac{d\phi}{dy}-p\frac{dv}{dy}\right)dy.$$

Consequently it follows that the coefficients of dx and dy in this equation are the differential coefficients of U with respect to x and y respectively, or

$$\frac{dU}{dx}=\tau\frac{d\phi}{dx}-p\frac{dv}{dx}, \text{ and } \frac{dU}{dy}=\tau\frac{d\phi}{dy}-p\frac{dv}{dy}.$$

But since dU is a perfect differential, we have

$$\frac{d}{dy}\left(\frac{dU}{dx}\right)=\frac{d}{dx}\left(\frac{dU}{dy}\right):$$

that is,

$$\frac{d}{dy}\left(\tau\frac{d\phi}{dx}-p\frac{dv}{dx}\right)=\frac{d}{dx}\left(\tau\frac{d\phi}{dy}-p\frac{dv}{dy}\right),$$

or finally, we are furnished with the elegant relation

$$\frac{d\tau}{dx}\frac{d\phi}{dy}-\frac{d\tau}{dy}\frac{d\phi}{dx}=\frac{dp}{dx}\frac{dv}{dy}-\frac{dp}{dy}\frac{dv}{dx} \quad . \quad . \quad . \quad (5)$$

the direct geometrical interpretation of which is that corresponding elements of area are equal whether referred to p and v, or τ and ϕ, as rectangular co-ordinates.

By choosing x and y as any pair of the four quantities p, v, τ, ϕ, this equation yields at once the following thermodynamic relations, connecting thermometric and calorimetric phenomena.

302. First Relation.—If ϕ and v be chosen as independent variables in the fundamental equation (5) of the preceding article, we obtain, replacing x by ϕ and y by v, and noticing that consequently $d\phi/dx=1$, and $dv/dy=1$, and that, in addition, since ϕ and v are supposed independent, we must have $d\phi/dy=0$ and $dv/dx=0$, so that (5) reduces to

$$\left(\frac{d\tau}{dv}\right)_\phi=-\left(\frac{dp}{d\phi}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

In this equation $d\tau$ is the change of temperature experienced by the substance in passing along an element of an adiabatic line (ϕ constant), and the left-hand member is the rate of change of temperature when the volume varies adiabatically, or the change of temperature per unit change of volume during an adiabatic transformation. In the right-hand member dp is the change of pressure caused by change of heat while the volume is kept constant, and the right-hand member is the change of pressure per unit change of entropy at constant volume.

The relation then asserts that during an adiabatic expansion the fall of temperature per unit increase of volume is equal to the

increase of pressure per unit increase of entropy at constant volume; or equal to the absolute temperature multiplied by the increase of pressure per (dynamical) unit increase of heat at constant volume, since $dQ = \tau d\phi$, and consequently the relation may be written in the form

$$\left(\frac{d\tau}{dv}\right)_\phi = -\tau\left(\frac{dp}{dQ}\right)_v$$

303. Second Relation. — Choosing τ and v for independent variables, we have in the general equation (5) $x = \tau$, $y = v$, and

$$\frac{d\tau}{dx}=1, \quad \frac{dv}{dy}=1, \quad \frac{d\tau}{dy}=0, \quad \frac{dv}{dx}=0,$$

and consequently the equation reduces to

$$\left(\frac{d\phi}{dv}\right)_\tau = \left(\frac{dp}{d\tau}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

which, being interpreted as before, means that the change of entropy per unit change of volume at constant temperature is equal to the change of pressure per unit change of temperature at constant volume, or writing it in the form

$$\left(\frac{dQ}{dv}\right)_\tau = \tau\left(\frac{dp}{d\tau}\right)_v,$$

we find that the change of heat per unit change of volume at constant temperature, or the latent heat of isothermal expansion, is equal to the absolute temperature multiplied by the change of pressure per unit change of temperature at constant volume.

For example, in the case of a body changing state at constant temperature, if L be the quantity of heat necessary to change unit mass of the substance from the first state into the second, and if v_1 and v_2 be the corresponding specific volumes of the substance, the whole change of volume is $v_2 - v_1$ (supposing the volume to be greater in the second condition than in the first), and hence the change of heat per unit change of volume is $L/(v_2 - v_1)$, and the equation becomes

$$\frac{L}{v_2 - v_1} = \tau\left(\frac{dp}{d\tau}\right)_v.$$

304. Third Relation. — Choosing p and ϕ for independent variables, we have $x = p$, $y = \phi$,

$$\frac{dp}{dx}=1, \quad \frac{d\phi}{dy}=1, \quad \frac{d\phi}{dx}=0, \quad \frac{dp}{dy}=0,$$

and equation (5) reduces to

$$\left(\frac{d\tau}{dp}\right)_\phi = \left(\frac{dv}{d\phi}\right)_p \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

which asserts that the change of temperature per unit increase of pressure during an adiabatic transformation is equal to the change of volume per unit increase of entropy under constant pressure. Or writing the relation in the form

$$\left(\frac{d\tau}{dp}\right)_\phi = \tau\left(\frac{dv}{dQ}\right)_p,$$

we find that the adiabatic rate of change of temperature with pressure is equal to the absolute temperature multiplied by the increase of volume per unit of heat supplied under constant pressure.

This relation also leads to the final equation of the preceding article.

305. Fourth Relation.—If we now take τ and p as independent variables, we have $x=\tau$, $y=p$,

$$\frac{d\tau}{dx}=1, \quad \frac{dp}{dy}=1, \quad \frac{d\tau}{dy}=0, \quad \frac{dp}{dx}=0,$$

and the fundamental equation reduces to

$$\left(\frac{d\phi}{dp}\right)_\tau = -\left(\frac{dv}{d\tau}\right)_p \quad . \quad . \quad \text{(IV)}$$

which implies that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature under constant pressure—that is, the expansion av. Writing the relation in the form

$$\left(\frac{dQ}{dp}\right)_\tau = -\tau\left(\frac{dv}{d\tau}\right)_p = -\tau va,$$

we see that the heat given out by the substance per unit increase of pressure at constant temperature is equal to the continued product of the absolute temperature, the volume, and the expansibility.

From this formula it follows that if a is positive—that is, if the substance expands with heating—then dQ/dp must be negative; or, in other words, a quantity of heat must be taken away from the body in order to keep its temperature constant when the pressure is increased. It follows, therefore, that increase of pressure is accompanied by a development of heat in the case of bodies which expand on being heated, and similarly increase of pressure will produce a lowering of temperature in the case of bodies which contract when heated.

These theoretical conclusions have been confirmed by many experiments. Thus Joule[1] found that water when suddenly compressed

[1] Joule, *Phil. Trans.*, 1859; *Scientific Papers*, p. 474.

at temperatures above 4° C. showed an increase of temperature, while at temperatures below 4° the opposite effect was produced. The liquid was enclosed in a strong vessel furnished with a cylinder in which a piston worked, and the pressure could be suddenly changed by loading the piston with weights. The change of temperature was measured by a thermoelectric couple of copper and iron wires, one junction of which was placed in the middle of the liquid under examination, and the other in a bath of water. Sperm oil was also examined, and the experimental results in all cases were in close accord with the numbers derived from theory.

Thermal effects of compression.

The effect of suddenly placing a wire or a bar of any substance under tension is the same as suddenly reducing the pressure (a tension being a negative pressure), so that wires of such substances as iron, copper, lead, etc., when suddenly stretched, show a cooling effect, while vulcanised india-rubber and wet bay wood were found by Joule to exhibit a heating effect.

306. Fifth and Sixth Relations. — The foregoing thermodynamic equations are generally known as "the four thermodynamic equations." Two other relations may be obtained immediately from equation (5) by choosing p and v, or τ and ϕ, for independent variables. Thus, if p and v be chosen, we have

$$\frac{dp}{dx}=1, \quad \frac{dv}{dy}=1, \quad \frac{dp}{dy}=0, \quad \frac{dv}{dx}=0,$$

and the fundamental equation (5) becomes

$$\left(\frac{d\tau}{dp}\right)_v\left(\frac{d\phi}{dv}\right)_p-\left(\frac{d\tau}{dv}\right)_p\left(\frac{d\phi}{dp}\right)_v=1 \quad . \quad . \quad . \quad . \quad \text{(V)}$$

In like manner, if τ and ϕ be chosen as independent variables, we have

$$\frac{d\tau}{dx}=1, \quad \frac{d\phi}{dy}=1, \quad \frac{d\tau}{dy}=0, \quad \frac{d\phi}{dx}=0,$$

and equation (5) reduces to

$$\left(\frac{dp}{d\tau}\right)_\phi\left(\frac{dv}{d\phi}\right)_\tau-\left(\frac{dp}{d\phi}\right)_\tau\left(\frac{dv}{d\tau}\right)_\phi=1 \quad . \quad . \quad . \quad . \quad \text{(VI)}$$

an equation which may be directly deduced from (V) by substituting in it from the four thermodynamic relations.

307. The Four Thermodynamic Formulæ.—The four thermodynamic formulæ deduced above as particular cases of the general equation of Art. 301 may also be deduced directly by writing the equation

$$dU = \tau d\phi - pdv \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in the equivalent forms—

$$d(U - \tau\phi) = -\phi d\tau - pdv \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$d(U + pv) = \tau d\phi + vdp \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$d(U - \tau\phi + pv) = vdp - \phi d\tau \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus, from (1), it follows that

$$\left(\frac{dU}{d\phi}\right)_v = \tau, \quad \text{and} \quad \left(\frac{dU}{dv}\right)_\phi = -p \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the first of which expresses that the absolute temperature measures the increase of internal energy per unit change of entropy at constant volume, or that the change of internal energy at constant volume is equal to the heat received, and the second expresses that the pressure measures the decrease of internal energy per unit increase of volume during adiabatic expansion. Differentiating the first of the equations (5) with respect to v, and the second with respect to ϕ, we have

$$\left(\frac{d\tau}{dv}\right)_\phi = -\left(\frac{dp}{d\phi}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

which is the first thermodynamic relation.

Similarly, from equation (2), if we write $U - \tau\phi = \mathcal{J}$, we have

$$\left(\frac{d\mathcal{J}}{d\tau}\right)_v = -\phi, \quad \text{and} \quad \left(\frac{d\mathcal{J}}{dv}\right)_\tau = -p,$$

with corresponding interpretations, and from these it follows that

$$\left(\frac{d\phi}{dv}\right)_\tau = \left(\frac{dp}{d\tau}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

which is the second relation.

So also, if we write $U + pv = \mathcal{J}'$, equation (3) gives us

$$\left(\frac{d\mathcal{J}'}{d\phi}\right)_p = \tau, \quad \text{and} \quad \left(\frac{d\mathcal{J}'}{dp}\right)_\phi = v.$$

Hence

$$\left(\frac{d\tau}{dp}\right)_\phi = \left(\frac{dv}{d\phi}\right)_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

which is the third relation.

Finally, writing $U - \tau\phi + pv = \Phi$, we have from equation (4)

$$\left(\frac{d\Phi}{dp}\right)_\tau = v, \quad \text{and} \quad \left(\frac{d\Phi}{d\tau}\right)_p = -\phi,$$

therefore

$$\left(\frac{dv}{d\tau}\right)_p = -\left(\frac{d\phi}{dp}\right)_\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

which is the fourth thermodynamic relation.

308. General Equations. — In the foregoing investigations the only external force acting on the body was supposed to be a uniform normal pressure p. In the general case the energy equation will be

$$dQ = dU + dW \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which, with the relation $dQ = \tau d\phi$, may be written in the form

$$dU = \tau d\phi - dW \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now if x and y be any two independent variables which determine the condition of the body, we have

$$d\phi = \left(\frac{d\phi}{dx}\right)_y dx + \left(\frac{d\phi}{dy}\right)_\tau dy,$$

and

$$dW = \left(\frac{dW}{dx}\right)_y dx + \left(\frac{dW}{dy}\right)_x dy.$$

It is to be remembered, however, that dW is not a perfect differential, and that consequently $\frac{d}{dx}\left(\frac{dW}{dy}\right)$ is not equal to $\frac{d}{dy}\left(\frac{dW}{dx}\right)$.

Substituting for $d\phi$ and dW in equation (2), we have

$$dU = \left(\tau\frac{d\phi}{dx} - \frac{dW}{dx}\right)dx + \left(\tau\frac{d\phi}{dy} - \frac{dW}{dy}\right)dy,$$

consequently

$$\frac{dU}{dx} = \tau\frac{d\phi}{dx} - \frac{dW}{dx}, \quad \text{and} \quad \frac{dU}{dy} = \tau\frac{d\phi}{dy} - \frac{dW}{dy} \quad . \quad . \quad . \quad . \quad (3)$$

But dU is a perfect differential, therefore

$$\frac{d}{dy}\left(\tau\frac{d\phi}{dx} - \frac{dW}{dx}\right) = \frac{d}{dx}\left(\tau\frac{d\phi}{dy} - \frac{dW}{dy}\right),$$

which, since $d\phi$ is also a perfect differential, reduces to

$$\frac{d\tau}{dx}\frac{d\phi}{dy} - \frac{d\tau}{dy}\frac{d\phi}{dx} = \frac{d}{dx}\left(\frac{dW}{dy}\right) - \frac{d}{dy}\left(\frac{dW}{dx}\right).$$

The right-hand member of this equation is termed by Clausius[1] "the work difference referred to xy," and is denoted by the symbol D_{xy}.

This may be regarded as the general differential equation for ϕ, and when the only force is a uniform external pressure it reduces to the equation of Art. 301.

In the same manner, by eliminating ϕ from equations (3), we obtain a general differential equation for U. Thus

$$\frac{d\phi}{dx} = \frac{1}{\tau}\left(\frac{dU}{dx} + \frac{dW}{dx}\right), \quad \text{and} \quad \frac{d\phi}{dy} = \frac{1}{\tau}\left(\frac{dU}{dy} + \frac{dW}{dy}\right),$$

[1] Clausius, *Mechanical Theory of Heat*, p. 114.

and consequently, since $d\phi$ is a perfect differential, we have

$$\frac{d}{dy}\left(\frac{1}{\tau}\frac{dU}{dx}+\frac{1}{\tau}\frac{dW}{dx}\right)=\frac{d}{dx}\left(\frac{1}{\tau}\frac{dU}{dy}+\frac{1}{\tau}\frac{dW}{dy}\right),$$

which reduces to

$$\frac{d\tau}{dx}\frac{dU}{dy}-\frac{d\tau}{dy}\frac{dU}{dx}=\tau^2\left[\frac{d}{dx}\left(\frac{1}{\tau}\frac{dW}{dy}\right)-\frac{d}{dy}\left(\frac{1}{\tau}\frac{dW}{dx}\right)\right].$$

When the only external force is a uniform pressure p, this becomes

$$\frac{d\tau}{dx}\frac{dU}{dy}-\frac{d\tau}{dy}\frac{dU}{dx}=\tau^2\left[\frac{d(p/\tau)}{dx}\frac{dv}{dy}-\frac{d(p/\tau)}{dy}\frac{dv}{dx}\right],$$

and when the variables are p and v, this becomes

$$\tau-p\frac{d\tau}{dp}=\frac{d\tau}{dp}\frac{dU}{dv}-\frac{d\tau}{dv}\frac{dU}{dp}.$$

Examples

1. Apply the relation (5) to prove that the difference of the specific heats of any substance may be expressed in the form

$$C_p-C_v=\tau\left(\frac{dp}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p=-\frac{\tau\left(\frac{dp}{d\tau}\right)_v^2}{\left(\frac{dp}{dv}\right)_\tau}.$$

[We have

$$C_p-C_v=\tau\left[\left(\frac{d\phi}{d\tau}\right)_p-\left(\frac{d\phi}{d\tau}\right)_v\right]$$

$$=\tau\left(\frac{dp}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p\left[\left(\frac{d\tau}{dp}\right)_v\left(\frac{d\phi}{dv}\right)_p-\left(\frac{d\tau}{dv}\right)_p\left(\frac{d\phi}{dp}\right)_v\right],$$ therefore, etc.]

2. Prove that the ratio of the adiabatic and isothermal elasticities of any substance is the same as the ratio of the two specific heats.

[We have

$$E_\phi=-v\left(\frac{dp}{dv}\right)_\phi,\quad\text{and } E_\tau=-v\left(\frac{dp}{dv}\right)_\tau.$$

Hence

$$\frac{E_\phi}{E_\tau}=\frac{\left(\frac{dp}{d\tau}\right)_\phi\left(\frac{d\tau}{dv}\right)_\phi}{\left(\frac{dp}{d\phi}\right)_\tau\left(\frac{d\phi}{dv}\right)_\tau}=\frac{\left(\frac{d\phi}{dv}\right)_p\left(\frac{dp}{d\phi}\right)_v}{\left(\frac{d\tau}{dv}\right)_p\left(\frac{dp}{d\tau}\right)_v}$$

in virtue of the thermodynamic relations.

Hence

$$\frac{E_\phi}{E_\tau}=\frac{\left(\frac{d\phi}{d\tau}\right)_p}{\left(\frac{d\phi}{d\tau}\right)_v}=\frac{\left(\frac{dQ}{d\tau}\right)_p}{\left(\frac{dQ}{d\tau}\right)_v}=\frac{C_p}{C_v}.\ ]$$

3. Prove that

$$dQ=C_p\left(\frac{d\tau}{dv}\right)_p dv+C_v\left(\frac{d\tau}{dp}\right)_v dp.$$

[The first member of the right-hand side is the quantity of heat required to be added to the substance while its temperature changes by $d\tau$, and the volume changes by dv under constant pressure. Similarly the second member is the quantity of heat required to be added while the volume is kept constant. The sum of the two is the whole quantity required when both volume and pressure vary.

Otherwise thus—

$$dQ=\left(\frac{dQ}{dv}\right)_p dv+\left(\frac{dQ}{dp}\right)_v dp=\left(\frac{dQ}{d\tau}\frac{d\tau}{dv}\right)_p dv+\left(\frac{dQ}{d\tau}\frac{d\tau}{dp}\right)_v dp$$

$$=C_p\left(\frac{d\tau}{dv}\right)_p dv+C_v\left(\frac{d\tau}{dp}\right)_v dp.$$

In the case of a perfect gas $pv=R\tau$, and we have

$$\frac{dQ}{\tau}=C_p\frac{dv}{v}+C_v\frac{dp}{p},$$

which, when $dQ=0$, gives $pv^\gamma=\text{const.}$]

4. Substituting this value of dQ in the equations $dQ=dU+pdv$, and $dQ=\tau d\phi$, show that, p and v being independent variables,

$$\frac{d}{dv}\left(C_v\frac{d\tau}{dp}\right)=\frac{d}{dp}\left(C_p\frac{d\tau}{dv}-p\right),$$

$$\frac{d}{dv}\left(\frac{C_v}{\tau}\frac{d\tau}{dp}\right)=\frac{d}{dp}\left(\frac{C_p}{\tau}\frac{d\tau}{dv}\right)$$

Hence deduce the relation

$$C_p-C_v=\tau\left(\frac{dp}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p.$$

5. If dQ be the quantity of heat absorbed during an isothermal expansion, prove that

$$dQ=\left(C_p-C_v\right)\left(\frac{d\tau}{dv}\right)_p dv.$$

[This follows from the above expression for dQ, Ex. 3, together with the isothermal condition

$$d\tau=\left(\frac{d\tau}{dp}\right)_v dp+\left(\frac{d\tau}{dv}\right)_p dv=0.]$$

6. Assuming Clapeyron's equation for an isothermal transformation,

$$dQ=\frac{1}{f(\theta)}\left(\frac{dp}{d\theta}\right)_v dv,$$

where $f(\theta)$ is some unknown function of the temperature centigrade, we have, by equating this value of dQ to that of Ex. 5,

$$(C_p-C_v)\left(\frac{d\tau}{dv}\right)_p=\frac{1}{f(\theta)}\left(\frac{dp}{d\theta}\right)_v.$$

But by Ex. 1,

$$(C_p-C_v)\left(\frac{d\tau}{dv}\right)_p=\tau\left(\frac{dp}{d\tau}\right)_v,$$

therefore

$$f(\theta)=\frac{1}{\tau}\frac{d\tau}{d\theta},$$

and

$$dQ=\tau\left(\frac{dp}{d\tau}\right)_v dv,$$

which is the second thermodynamic relation.

7. Writing the equation for dQ in the form

$$dQ = C_v d\tau + l dv,$$

where l is the latent heat of isothermal expansion, prove that

$$l = \tau\frac{dp}{d\tau}, \quad \text{and } \frac{dC_v}{dv} = \tau\frac{d^2p}{d\tau^2}.$$

[The equation is equivalent to

$$d\phi = \frac{1}{\tau}(C_v d\tau + l dv),$$

and consequently

$$\frac{d}{dv}\left(\frac{C_v}{\tau}\right) = \frac{d}{d\tau}\left(\frac{l}{\tau}\right);$$

also

$$dU = C_v d\tau + l dv - p dv,$$

therefore

$$\frac{dC_v}{dv} = \frac{d}{d\tau}(l - p);$$

consequently by comparison we obtain the relations in question. For a unit mass of liquid converted at constant temperature into vapour we have

$$\frac{L}{v_2 - v_1} = \tau\frac{dp}{d\tau}.]$$

8. Prove that

$$dQ = C_v d\tau - (C_p - C_v)\frac{d\tau}{dv}dv.$$

[We have by Ex. 3

$$dQ = C_p\frac{d\tau}{dp}dp + C_v\frac{d\tau}{dv}dv.$$

But

$$d\tau = \frac{d\tau}{dp}dp + \frac{d\tau}{dv}dv;$$

therefore by substituting for $\frac{d\tau}{dp}dp$ we obtain the relation in question.

This relation compared with that of the preceding example shows us that

$$l = -(C_p - C_v)\frac{d\tau}{dv} = \tau\frac{dp}{d\tau}. \quad \text{See Ex. 1.]}$$

9. Writing the equation for dQ in the form

$$dQ = C_p d\tau + l' dp,$$

prove that

$$l' = -\tau\frac{dv}{d\tau} = -\tau v a, \quad \text{and } \frac{dC_p}{dp} = -\tau\frac{d^2v}{d\tau^2}.$$

10. Prove by direct transformation that the equation

$$\frac{dC_v}{dv} = \tau\frac{d^2p}{d\tau^2}$$

is equivalent to

$$(C_p - C_v) = \tau\left(\frac{dp}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p.$$

11. In the case of a saturated vapour the pressure is independent of the volume, and consequently the equation

$$\frac{dC_v}{dv}=\tau\frac{d^2p}{d\tau^2}$$

leads to the equation

$$C_v=\tau v\frac{d^2p}{d\tau^2}+f(\tau).$$

12. Show that the relations

$$\frac{d}{d\tau}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{d\tau}\right)=\frac{dp}{d\tau},$$

$$\frac{d}{d\tau}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{d\tau}\right)=\frac{1}{\tau}\frac{dQ}{dv},$$

$$\frac{d}{dv}\left(\frac{dQ}{d\tau}\right)=\tau\frac{d^2p}{d\tau^2}$$

are equivalent forms of the second thermodynamic relation.

13. In the same manner prove that

$$\frac{d}{d\tau}\left(\frac{dQ}{dp}\right)-\frac{d}{dp}\left(\frac{dQ}{d\tau}\right)=-\frac{dv}{d\tau},$$

$$\frac{d}{d\tau}\left(\frac{dQ}{dp}\right)-\frac{d}{dp}\left(\frac{dQ}{d\tau}\right)=\frac{1}{\tau}\frac{dQ}{dp},$$

$$\frac{d}{dp}\left(\frac{dQ}{d\tau}\right)=-\tau\frac{d^2v}{d\tau^2}$$

are equivalent forms of the fourth relation.

14. Show that

$$\frac{d}{dp}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dp}\right)=1=\frac{1}{\tau}\left(\frac{d\tau}{dp}\frac{dQ}{dv}-\frac{d\tau}{dv}\frac{dQ}{dp}\right)$$

are equivalent forms of the fifth relation.

15. If

$$D_{xy}=\frac{d}{dx}\left(\frac{dW}{dy}\right)-\frac{d}{dy}\left(\frac{dW}{dx}\right),$$

$$=D_{\xi\eta}\frac{d}{d\xi}\left(\frac{dW}{d\eta}\right)-\frac{d}{d\eta}\left(\frac{dW}{d\xi}\right),$$

prove that

$$D_{\xi\eta}=\left(\frac{dx}{d\xi}\frac{dy}{d\eta}-\frac{dx}{d\eta}\frac{dy}{d\xi}\right)D_{xy},$$

and similarly if

$$\Delta_{xy}=\tau^2\left[\frac{d}{dx}\left(\frac{1}{\tau}\frac{dW}{dy}\right)-\frac{d}{dy}\left(\frac{1}{\tau}\frac{dW}{dx}\right)\right],$$

prove that

$$\Delta_{\xi\eta}=\left(\frac{dx}{d\xi}\frac{dy}{d\eta}-\frac{dx}{d\eta}\frac{dy}{d\xi}\right)\Delta_{xy}.$$

16. Prove that when the only force is a uniform external pressure

$$dQ=\frac{\tau}{C_p-C_v}\left[C_p\left(\frac{dp}{d\tau}\right)_v dv+C_v\left(\frac{dv}{d\tau}\right)_p dp\right].$$

[We have

$$dQ=\left(\frac{dQ}{d\tau}\right)_v d\tau+\left(\frac{dQ}{dv}\right)_\tau dv=C_v d\tau+\tau\left(\frac{dp}{d\tau}\right)_v dv$$

by the second thermodynamic relation.

Similarly

$$dQ=\left(\frac{dQ}{d\tau}\right)_p d\tau+\left(\frac{dQ}{dp}\right)_\tau dp=C_p d\tau-\tau\left(\frac{dv}{d\tau}\right)_p dp$$

by the fourth thermodynamic relation.

Eliminating $d\tau$ by means of these two equations, we obtain the expression in question.

In the case of a perfect gas the corresponding equations are

$$dQ=C_v d\tau+\frac{R\tau}{v}dv,$$

$$dQ=C_p d\tau-\frac{R\tau}{p}dp,$$

$$dQ=\frac{C_p}{C_p-C_v}pdv+\frac{C_v}{C_p-C_v}vdp.\Big]$$

17. Find the relation between the specific heats of a gas, if the quantity of heat Q required for a transformation of a gas depends only upon the initial and final states.

[We have the foregoing equation

$$(C_p-C_v)dQ=C_v vdp+C_p pdv.$$

Hence if dQ is the complete differential of a function of p and v, we have

$$\frac{d}{dv}\left(\frac{C_v v}{C_p-C_v}\right)=\frac{d}{dp}\left(\frac{C_p p}{C_p-C_v}\right) \quad . \quad . \quad . \quad . \quad (1)$$

This equation cannot be satisfied if C_p and C_v are different constants, but if they be considered as unknown functions of p there is an infinite number of solutions.

One of historic importance is found in the supposition that $C_p-C_v=\text{const.}=R$, then equation (1) becomes

$$v\frac{dC_v}{dv}-p\frac{dC_v}{dp}=R,$$

or

$$C_v=R\log(v)+F(pv) \quad . \quad . \quad . \quad . \quad (2)$$

$F(pv)$ being an arbitrary function of pv, and consequently of the temperature τ. Hence, if for the same temperature each of the two specific heats (the difference of which is supposed const.) increases proportionately to the logarithm of the volume, then heat may be regarded as a substance, the presence of which in greater or less quantity determines the thermal state of a body. Accepting this hypothesis, which is contradicted by all the facts, we may calculate the quantity of heat in the gas.

Thus writing $F(pv)=\phi'(pv)$ for facility, we have

$$C_v=R\log v+\phi'(pv),$$

$$C_p=C_v+R=R+R\log v+\phi'(pv).$$

Therefore

$$RdQ=C_v vdp+C_p pdv$$

$$=\phi'(pv)(vdp+pdv)+Rpdv+R\log v(vdp+pdv);$$

hence

$$RQ=\phi(pv)+Rpv\log v,$$

or

$$Q=\psi(\tau)+R\tau\log v,$$

the function ψ being left indeterminate.

Carnot regarded heat as a substance, and consequently admitted that the specific heats increased as the logarithm of the volume. This, however, remained to be tested by experiment.]

18. Show that the quadrilateral area between the lines $\tau=\alpha$, $\tau=\alpha+d\alpha$ and $\phi=\beta$, $\phi=\beta+d\beta$ is

$$\frac{d\alpha d\beta}{\frac{d\tau}{dp}\frac{d\phi}{dv}-\frac{d\tau}{dv}\frac{d\phi}{dp}},$$

and hence show that when quantities of heat are measured in thermal units

$$\frac{d\tau}{dp}\frac{d\phi}{dv}-\frac{d\tau}{dv}\frac{d\phi}{dp}=\frac{1}{J}.$$

[Cf. Equation (5), p. 638.]

19. Employ the equation of Ex. 3 to prove that

$$C_p-C_v=\tau\left(\frac{dp}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p.$$

[Dividing both sides by τ we have

$$\frac{d\phi}{dp}=\frac{C_v}{\tau}\frac{d\tau}{dp},\quad \frac{d\phi}{dv}=\frac{C_p}{\tau}\frac{d\tau}{dv},$$

which, by means of the final equation of the preceding example, reduces as required.]

20. Prove that if a be the coefficient of expansion the element of heat communicated to a body may be expressed in the form

$$dQ=C_pd\tau-av\tau dp.$$

[We have

$$dQ=\left(\frac{dQ}{d\tau}\right)_p d\tau+\left(\frac{dQ}{dp}\right)_\tau dp,$$

and by the fourth thermodynamic relation this transforms into the required expression.]

21. Prove that

$$d(U+pv)=C_pd\tau+v(1-a\tau)dp.$$

22. Deduce the relations—

$$\frac{dp}{dU}=\frac{d\tau}{dU}\frac{d\phi}{dv}-\frac{d\tau}{dv}\frac{d\phi}{dU}$$

$$\frac{dv}{dU}=\frac{d\phi}{dU}\frac{d\tau}{dp}-\frac{d\phi}{dp}\frac{d\tau}{dU}$$

$$\frac{d\tau}{dU}=\frac{dp}{dU}\frac{dv}{d\phi}-\frac{dp}{d\phi}\frac{dv}{dU}$$

$$\frac{d\phi}{dU}=\frac{dv}{dU}\frac{dp}{d\tau}-\frac{dv}{d\tau}\frac{dp}{dU}.$$

[These follow from equation (5), p. 638, by taking as independent variables U and one of the quantities v, p, ϕ, τ.]

SECTION VI

CHANGE OF STATE

309. The Fundamental Equations.—The general phenomena attending the change of state of matter have been described in Chapter V., and we shall now consider them from the point of view of the thermodynamic theory, and deduce the laws applying to the passage of matter from any one of its three typical states to any other. Our results apply alike to the passage from the liquid to the solid state, or from either of these states to the condition of saturated vapour; but for the sake of definiteness we may keep in view one particular change of state, say that of a liquid into its saturated vapour. The characteristic of such a transformation is that the pressure depends on the temperature alone, and not on the volume, so that p and τ cannot be chosen as independent variables defining the condition of the substance.

Let us take the case of a unit mass of any substance existing partly in one state (say liquid) and partly in another (saturated vapour), and let v_1 and v_2 be the specific volumes of the substance in the first and second states respectively. Then if the quantity of matter in the second state be m, the quantity in the first state will be $1-m$, and the whole volume of the mixture will be

$$v=(1-m)v_1+mv_2.$$

When v and p, or v and τ, are known, v_1 and v_2 can be expressed in terms of them, and the quantity m can be determined. When a further quantity dm of the mass changes state, the quantity of heat necessary to effect the transformation is $dQ=Ldm$, where L is the latent heat of change of state, and in this case the pressure is supposed constant, so that the volume v of the mass changes accordingly. If, however, the whole volume v be kept constant, the transformation of dm will entail a change of temperature and a corresponding change of pressure throughout the mass; so that if s_1 be the specific heat of the substance in the first state, and s_2 that in the second, as explained below (pp. 651-2),

the transformation of a small quantity dm of the substance will produce a small change of temperature $d\tau$ throughout the whole mass, and the quantity of heat necessary to the operation will be

$$dQ = Ldm + \{s_1(1-m)+s_2m\}d\tau \quad . \quad . \quad . \quad . \quad (1)$$

But $dQ = \tau d\phi$, and consequently

$$d\phi = \frac{L}{\tau}dm + \frac{s_1(1-m)+s_2m}{\tau}d\tau. \quad . \quad . \quad . \quad . \quad (2)$$

We have thus the otherwise obvious relations [1]

$$\left(\frac{d\phi}{dm}\right)_\tau = \frac{L}{\tau}, \text{ and } \left(\frac{d\phi}{d\tau}\right)_m = \frac{s_1(1-m)+s_2m}{\tau} \quad . \quad . \quad . \quad (3)$$

Now $d\phi$ is a perfect differential, and therefore these equations give us

$$\frac{d}{dm}\left\{\frac{s_1(1-m)+s_2m}{\tau}\right\} = \frac{d}{d\tau}\left(\frac{L}{\tau}\right);$$

that is,

$$s_2 - s_1 = \tau\frac{d}{d\tau}\left(\frac{L}{\tau}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The first of the equations (3) is merely a statement of the fact that under constant pressure (or temperature) $dQ = Ldm$, and it at once leads to another fundamental equation. For since the whole change of volume per unit mass in passing from one state to the other is $v_2 - v_1$, we have for the change of volume, when the quantity dm is transformed under constant pressure, $dv = (v_2 - v_1)dm$. Hence the first of the equations (3) gives

$$(v_2 - v_1)\left(\frac{d\phi}{dv}\right)_\tau = \frac{L}{\tau},$$

or by the second thermodynamic relation (Art. 303),

$$\frac{L}{\tau} = (v_2 - v_1)\left(\frac{dp}{d\tau}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If the change of state takes place in such a way that p is independent of v, the suffix may be omitted in $dp/d\tau$.

Equations (4) and (5) are the fundamental thermodynamic formulæ applying to the passage of a substance from any one of the three states of matter to any other, whether it be liquefaction, vaporisation, or sublimation. The quantities s_1 and s_2 are the specific heats of the substance in the two states under the conditions of pressure and volume at which the transformation takes place, and in the operation considered above they agree neither with the specific heat at constant volume nor with that under constant pressure; but in the case of the liquid or solid the specific heat under constant pressure may be used without serious

[1] Obvious, since when τ is constant $dQ = Ldm = \tau d\phi$, which is the first relation, and when m is constant $dQ = s_1(1-m)d\tau + s_2md\tau = \tau d\phi$, which is the second.

error, as the dilatation and external work are small. In the case of the saturated vapour, however, the specific heat employed here is the quantity of heat required to raise the temperature of unit mass of the saturated vapour one degree, while the pressure is so varied that the mass is kept at the saturation point throughout the operation. This quantity will be considered more fully later on (p. 655).

If the specific heats of the substance be known in both states, then equation (4) furnishes us with a knowledge of the variations of the latent heat with temperature, or if the specific heat in one state be known, and if the latent heat be known as a function of the temperature, the equation may be employed to determine the specific heat of the substance in the other state.

On the other hand, if the pressure of the saturated vapour be known in terms of the temperature, equation (5) yields the specific volume (or density) of the saturated vapour at all temperatures when the density of the liquid and the latent heat are known.[1] So also, since L and τ are both positive, it follows that if v_2 is greater than v_1, then dp and $d\tau$ must have the same sign, but if v_2 be less than v_1, then dp and $d\tau$ must have opposite signs. In other words, if a substance passes from one state to another in which the specific volume is greater, then an increase of pressure raises the temperature at which this transformation will take place. This happens in the case of liquids passing into vapour, or in the case of solids, which expand in melting, and is expressed by saying that increase of pressure raises the boiling point or melting point. If, however, the substance contracts in passing from the first state to the second, then if dp be positive, $d\tau$ will be negative, and an increase of pressure will lower the temperature at which the transformation can occur. A notable example of this occurs in the case of ice (Art. 158), which we have seen contracts in melting, and consequently has its melting point lowered by increase of pressure. The dynamical theory thus leads us to anticipate all the phenomena treated of in Art. 159.

[1] Clausius has deduced the values of the specific volume (or density) of saturated steam at various temperatures by this method, and has shown that grave errors are introduced when the density of a saturated vapour is deduced from that of the superheated vapour, under the supposition that it obeys the laws of a perfect gas (*Mechanical Theory of Heat*, p. 143). In this formula L is measured in work units, so that if all the quantities involved have been determined experimentally, the formula yields the value of the dynamical equivalent, L being known in thermal units. In this manner M. Pérot (*Ann. de Chimie*, 6[e], tom. xiii. p. 145, 1888), having determined the densities of saturated water vapour and ether vapour, deduced the value 424 for J, thus verifying the formula. In a similar manner it has been verified by M. Mathias (*Ann. de Chimie*, 6[e], tom. xxi. p. 69, 1890). For another mode of verification, see Bertrand's *Thermodynamics*, p. 155.

When $v_2 = v_1$ the equation shows that either $L = 0$ or else $dp/d\tau$ is infinite. The former condition is approached in the case of a liquid passing into vapour when the temperature approaches that of the critical point; and in the case of fusion, where $v_2 - v_1$ is small, the coefficient of increase of pressure with temperature is large, and the latter condition is approached.

Examples

1. Find the lowering of the freezing point of water per atmosphere increase of pressure, taking the latent heat of ice to be 80, the specific volume of ice being 1·087, and that of water at 0° C. being unity.

[Here we have $v_2 - v_1 = 0{\cdot}087$, $\tau = 273$, $dp = 1033$ grammes, while L expressed in dynamical units is 80×42700, hence

$$\frac{80 \times 42700}{273} = 0{\cdot}087 \frac{1033}{d\tau},$$

or

$$d\tau = \frac{1033 \times 273 \times 0{\cdot}087}{80 \times 42700} = 0{\cdot}0072.]$$

2. In the case of paraffin the latent heat in thermal units is 35·35, $v_2 - v_1 = 0{\cdot}125$, $\tau = 325{\cdot}7$, find the change of temperature per atmosphere in the melting point.

[*Ans.* $d\tau = 0{\cdot}028$.

Experiments on this substance gave M. Battelli[1] a mean change of 0°·03 C. per atmosphere.

3. In the case of naphthalene, if the latent heat in thermal units $= 35{\cdot}46$, $v_2 - v_1 = 0{\cdot}146$, $\tau = 352{\cdot}2$, find the change in the melting point per atmosphere.

[*Ans* $d\tau = 0{\cdot}035$.

As the equations (4) and (5) are of fundamental importance, the following instructive method of deducing them is added.

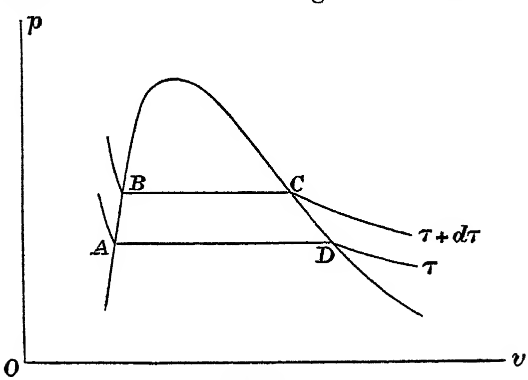

Fig. 178.

Let AD and BC (Fig. 178) represent the isothermal lines corre-

[1] M. A. Battelli, *Journal de Phys.*, tom. vi. p. 90, 1887.

sponding to two infinitely close temperatures τ and $\tau+d\tau$. Along the line AB the substance is all in the liquid state, and along the line CD it is all in the condition of saturated vapour. Now if a unit mass of the substance be supposed to describe the cycle ABCD, the quantity of heat absorbed in passing from A to B will be $s_1 d\tau$, and the quantity given out in passing from C to D will be $s_2 d\tau$, so that if L be the latent heat at the temperature τ, that at the temperature $\tau+d\tau$ will be

$$\mathrm{L}+\frac{d\mathrm{L}}{d\tau}d\tau,$$

and the total quantity of heat absorbed during the cycle will be

$$d\mathrm{Q}=s_1 d\tau+\mathrm{L}+\frac{d\mathrm{L}}{d\tau}d\tau-s_2 d\tau-\mathrm{L}=\left(s_1-s_2+\frac{d\mathrm{L}}{d\tau}\right)d\tau.$$

But $d\mathrm{Q}$ is the equivalent of the external work done — that is, of the area of the cycle, the length of which is v_2-v_1, and the breadth $\left(\frac{dp}{d\tau}\right)_v d\tau$.

Hence

$$d\mathrm{Q}=(v_2-v_1)\left(\frac{dp}{d\tau}\right)_v d\tau.$$

Consequently we have

$$s_1-s_2+\frac{d\mathrm{L}}{d\tau}=(v_2-v_1)\left(\frac{dp}{d\tau}\right)_v \quad . \quad . \quad . \quad . \quad (6)$$

Further, the change of entropy must be zero, since the substance has returned to its initial condition, therefore

$$\Sigma\frac{d\mathrm{Q}}{\tau}=\frac{s_1 d\tau}{\tau}+\frac{\mathrm{L}+\frac{d\mathrm{L}}{d\tau}d\tau}{\tau+d\tau}-\frac{s_2 d\tau}{\tau}-\frac{\mathrm{L}}{\tau}=0,$$

or

$$s_2-s_1=\frac{d\mathrm{L}}{d\tau}-\frac{\mathrm{L}}{\tau}=\tau\frac{d}{d\tau}\left(\frac{\mathrm{L}}{\tau}\right),$$

which is the same as equation (4). Combining this with (6) we obtain (5), or

$$\frac{\mathrm{L}}{\tau}=(v_2-v_1)\frac{dp}{d\tau}=s_1-s_2+\frac{d\mathrm{L}}{d\tau},$$

which express the two fundamental equations.

310. Internal and External Latent Heats.—When change of state occurs with change of volume the heat necessary to the transformation is the sum of two parts: one the equivalent of the external work done while the volume changes; and the other, which is sometimes called the "true latent heat," is spent in altering the internal energy of the substance. If the transformation takes place under a uniform pressure p, the heat spent in external work, or the *external* latent heat, is

$$\mathrm{L}_e=p(v_2-v_1),$$

and consequently the heat spent in doing internal work, or the *internal* latent heat, is

$$L_i = L - p(v_2 - v_1) = \tau(v_2 - v_1)\left(\frac{dp}{d\tau} - \frac{p}{\tau}\right),$$

or

$$L_i = \tau^2(v_2 - v_1)\frac{d}{d\tau}\left(\frac{p}{\tau}\right).$$

Thus for water at 100° C., $L_e = 40{\cdot}21$, and $L_i = 496{\cdot}29$.

311. Specific Heat of Saturated Vapour.—We now return to the consideration of the fundamental equation (4), which connects the difference of the specific heats with the temperature and the latent heat of change of state. In the case of the liquid and solid states the specific heats commonly considered are positive quantities, and the ordinary specific heat under constant pressure of the solid or liquid at the temperature in question may be used without appreciable error in dealing with this equation. In the case of the saturated vapour, however, the specific heat involved is neither that at constant pressure nor yet that at constant volume, but is the quantity of heat supplied to a unit mass of the saturated vapour when its temperature is raised 1° C., while at the same time the pressure and volume are varied in such a manner that the whole mass remains saturated.

Under such conditions the quantity of heat supplied will depend upon the amount of work done on or by the substance, while its volume is varied under pressure, so as to keep it saturated, and, as already pointed out (Art. 122), the specific heat under such circumstances may have any value, positive or negative, depending on the nature of the substance and the temperature in question. We must not be surprised, therefore, if we find that the specific heats of some saturated vapours are positive while others are negative, or that the specific heat of the same saturated vapour is positive at some temperatures and negative at others.

The meaning of the specific heat of a substance under certain conditions being positive is that, in order to change the temperature of unit mass of the substance 1° C. under the given conditions, a certain quantity of heat must be communicated to it while external work is done on or by the substance according to the nature of the given conditions, while if the specific heat is negative the external work, which must be done on the substance in consequence of the given conditions, is more than sufficient to raise the temperature of the mass 1° C., and therefore heat must be taken from the substance in order that the temperature may not rise above the required point.

Consequently, when it is said that the specific heat of a saturated

vapour of some given substance is negative, it is to be inferred that the work spent in compressing any mass of the saturated vapour to the volume which the same mass would occupy when existing as saturated vapour at a temperature 1° higher, would if converted into heat be more than sufficient to raise the temperature of the mass 1° C. In other words, the internal energy of a unit mass of the vapour at θ exceeds the internal energy of a unit mass at a temperature 1° lower by a quantity which is less than the work required to compress the mass at the lower temperature into the volume occupied at the higher.

Our fundamental equation

$$s_2 = s_1 + \frac{dL}{d\tau} - \frac{L}{\tau}$$

shows us that s_2 may be either positive or negative according to the magnitudes of the quantities involved in the right-hand member, and if we use the equation of Ex. 20, p. 649,

$$dQ = C_p d\tau - av\tau dp,$$

we are led to the same conclusion, for in the case of a saturated vapour p is a function of τ alone, and consequently we may write

$$dp = \frac{dp}{d\tau} d\tau,$$

so that we have for the specific heat

$$\frac{dQ}{d\tau} = C_p - av\tau \frac{dp}{d\tau},$$

a quantity which may be either positive or negative.

As an example we shall consider the important and interesting case of water vapour. For this substance Regnault found, as explained in Art. 175, for the total heat Q at any temperature θ

$$Q = L + \int_0^\theta s d\theta = 606{\cdot}5 + 0{\cdot}305\theta \tag{1}$$

where s is the mean specific heat of water between 0° and θ°. Hence

$$L = 606{\cdot}5 + 0{\cdot}305\theta - \int_0^\theta s d\theta,$$

and for water

$$s = 1 + 0{\cdot}00004\theta + 0{\cdot}0000009\theta^2,$$

therefore[1]

$$L = 606{\cdot}5 - 0{\cdot}695\theta - 0{\cdot}00002\theta^2 - 0{\cdot}0000003\theta^3.$$

[1] Clausius uses the shorter expression

$$L = 607 - 0{\cdot}708\theta,$$

and hence

$$s_2 = 0{\cdot}305 - \frac{607 - 0{\cdot}708\theta}{273 + \theta},$$

But by (1), if $d\tau$ be taken equal to $d\theta$ in accordance with the equation $\tau = 273 + \theta$ (p. 617), we have

$$\frac{dL}{d\tau} + s = 0\cdot305,$$

and hence by substitution in the fundamental formula we find for the saturated vapour

$$s_2 = 0\cdot305 - \frac{606\cdot5 - 0\cdot695\theta - 0\cdot00002\theta^2 - 0\cdot0000003\theta^3}{273 + \theta},$$

which is obviously negative for any moderate value of θ.

The following table contains the specific heats of the undermentioned saturated vapours, as deduced by Clausius from the results of Regnault's experiments, using the fundamental formula (4)—

Temperature.	0° C.	50°.	100°	150°.
Water vapour	−1·916	−1·465	−1·133	−0·676
Ether	+0·1057	+0·1222	+0·1309	+0·1344
Bisulphide of carbon . .	−0·1837	−0·1600	−0·1406	−0·1325
Chloroform	−0·1079	−0·0549	−0·0153	+0·0155
Bichloride of carbon . .	−0·0442	−0·0219	−0·0066	−0·0015
Aceton	−0·1482	−0·08832	−0·0515	−0·0223

The foregoing table shows that the specific heat of saturated water vapour is negative[1] at all moderate temperatures, and that within the same range the specific heat of ether vapour is positive.

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or

$$s_2 = 1\cdot013 - \frac{800\cdot3}{273 + \theta},$$

which gives values agreeing closely with those deduced from the longer expression.

[1] The fact that the specific heat of saturated water vapour is a negative quantity was discovered simultaneously by Rankine and Clausius in 1850. Previously the subject had been treated from the point of view of the caloric theory, according to which the so-called total heat (that is, the quantity of heat taken in by a body in passing from a given initial to a given final condition) depends only on the initial and final states, and may therefore be expressed completely as a function of the variables which define the condition of the body, depending in no way upon the manner in which the substance passes from the initial to the final state. This is

The numbers further show that the value of this quantity approaches zero in the case of water vapour as the temperature rises, and in the case of ether as the temperature falls. We are thus led to suspect that for each of these substances there is a temperature at which the specific heat of the saturated vapour vanishes, and that probably beyond this temperature an inversion occurs, and the specific heat changes sign, becoming positive in the case of water vapour and negative in the case of ether. This inversion is shown to actually occur in the case of chloroform, the specific heat of the vapour being positive above, and negative below, the temperature 123° C. We may therefore conclude that the specific heat of the saturated vapour of any substance may be either positive or negative according to the temperature. When the specific heat of a saturated vapour is negative adiabatic expansion will be accompanied by partial condensation, for if we suppose the mass to expand until its temperature falls by any given amount, a quantity of heat must be added to it, in order that it may remain just saturated at the lower temperature, and if this quantity be not supplied condensation must take place. In the same manner it follows that when the specific heat of a saturated vapour is positive, heat must be taken away from it, in order that it may

Inversion.

Effect of adiabatic expansion.

expressed by saying that dQ is a perfect differential, and hence, from equation (1), Art. 309, we have

$$\frac{dL}{d\tau}=\frac{d}{dm}\{s_2m+s_1(1-m)\}=s_2-s_1,$$

which gives

$$s_2=s_1+\frac{dL}{d\tau} \qquad (1)$$

Now Watt, who was the first to publish any distinct views on this subject, was led by his experiments to the conclusion that the sum of the free and latent heats is constant (Watt's *Law*, p. 307), and this is expressed by the equation

$$L+\int s_1 d\tau=\text{const.}, \text{ or } \frac{dL}{d\tau}+s_1=0 \qquad (2)$$

This combined with (1) leads to the conclusion that s_2 is zero, a result which was long believed to be true, and was expressed by saying that if a saturated vapour changes its volume in a vessel impermeable to heat it always remains saturated. Regnault's experiments (Art. 175), however, proved that Watt's law was false, and that

$$\frac{dL}{d\tau}+s_1=0{\cdot}305,$$

which, combined with (1), led to the conclusion that for water vapour $s_2=0{\cdot}305$, a positive quantity. Hence the idea arose that if saturated steam is compressed, heat must be supplied to it in addition to that generated by the compression, in order that it may remain throughout at the saturation point, and conversely, if saturated steam be allowed to expand in order to cool it, so that it may remain saturated during the expansion, a positive quantity of heat must be abstracted from it.

remain saturated as it cools, consequently during adiabatic expansion the vapour must become superheated.

Experiments of MM. Hirn and Cazin.

The fact that the specific heat of water vapour is negative is of particular interest on account of its importance in the theory of the steam-engine, and in 1862 Hirn verified experimentally that the sudden adiabatic expansion of dry saturated steam is accompanied by condensation. He allowed steam to pass gently from a boiler, in which it was generated under a pressure of 5 atmos., into a long copper cylinder, the ends of which were closed with parallel plates of glass. The steam was allowed to enter this cylinder until all the air and condensed water were driven out and the walls had attained the temperature of the steam. The exit tap of the cylinder was then shut and connection with the boiler was cut off. The cylinder was thus filled with dry saturated vapour at a pressure of 5 atmos., and when looked through from end to end appeared quite clear. The exit tap being suddenly opened, the pressure at once fell, and a dense cloud formed within the cylinder, which rendered it opaque to an observer looking through from end to end. This cloud, however, soon disappeared as the vapour, now at 100° C., rapidly absorbed heat from the walls of the cylinder (previously at 152° C.). No such condensation could be obtained when ether vapour was treated in the same way; but, on the other hand, this substance exhibited condensation when suddenly compressed.

These experiments were subsequently repeated with an improved form of apparatus by M. Cazin.[1] The cylinder was connected with another in which a piston worked, and the whole was placed in an oil-bath, the temperature of which could be varied at pleasure. By this arrangement saturated vapour in one cylinder could be allowed to suddenly expand into the other, or, when occupying both, could be suddenly compressed by moving the piston. A cloud was always formed by expansion in the case of steam but never by compression, and the same result was obtained with bisulphide of carbon. On the other hand, ether vapour always condensed during compression but never during expansion, showing that its temperature of inversion, as in the case of steam, was not within the limits of the experiments. In the case of chloroform the temperature of inversion appeared to be between 130° and 136° C., and in the case of benzine between 115° and 130° C.

From some recent experiments on the latent heats of the liquefiable gases—carbon dioxide, sulphurous acid, and protoxide of nitrogen—M.

[1] Cazin, *Ann. de Chimie et de Phys.*, 4e, tom. xix.; *Comptes Rendus*, tom. lxii. p. 56, 1866.

Mathias[1] concludes that, as the temperature approaches that of the critical point, the specific heat of every saturated vapour becomes negative, and increases indefinitely in absolute value. For the substances examined it appeared that the latent heat of vaporisation decreases as the temperature rises, and ultimately vanishes, as would be expected, at the critical point, so that if a curve be constructed, having latent heats for ordinates and temperatures for abscissæ, this curve will cut the axis of abscissæ at a point corresponding to the critical temperature. It was further found that this curve intersects the axis at right angles in all the cases examined, and consequently at the critical point we have

$$L=0, \quad \text{and } \frac{dL}{d\tau}=-\infty.$$

Hence it follows from the equation

$$s_2=s_1+\frac{dL}{d\tau}-\frac{L}{\tau}$$

that, at the critical temperature, we have $s_2=-\infty$.

If all substances behave in this way, then, in the neighbourhood of the critical point, the specific heat is negative for all saturated vapours. Now in all known cases s_2 increases with rise of temperature, and by the foregoing it decreases to $-\infty$ at the critical point, and must therefore pass through a maximum value at some temperature below the critical point. Consequently, if there be a point of inversion at ordinary temperatures at which s_2 passes from negative to positive values, there must also be a second point of inversion below the critical temperature at which it changes from positive to negative. There may then be two points of inversion, but if only one point of inversion exists it must be the latter.

Two inversions.

The negative value of the specific heat of steam, and the consequent condensation of this vapour when allowed to expand, appeared at first sight inconsistent with the long-known paradox that high-pressure steam escaping from a small orifice into the air will not burn the hand, or even the face; while, on the contrary, low-pressure steam (which is consequently at a lower temperature) inflicts horrible burns. This difficulty was explained by Lord Kelvin thus:[2] "The steam, in rushing through the orifice, produces mechanical effect which is immediately wasted in fluid friction, and consequently reconverted into heat, so that the issuing steam at the atmospheric pressure would have to part with as much heat to convert it into water at the temperature of 100°,

[1] Mathias, *Ann. de Chimie et de Phys.*, 6e, tom. xxi. p. 69, 1890.

[2] *Dynamical Theory of Heat.*

as it would have had to part with to have been condensed at the high pressure, and then cooled down to 100°, which, for a pound of steam initially saturated at the temperature t, is by Regnault's modification of Watt's law ·305 $(t-100)$ more heat than a pound of saturated steam at 100° would have to part with to be reduced to the same state; and the issuing steam must, therefore, be above 100° in temperature, and dry." The thermal effect of fluid friction alluded to in this statement is considered in Art. 327.

312. The Triple Point.—When an enclosure is filled by a substance which is partly liquid, and partly in the state of saturated vapour, the pressure is a function of the temperature alone, and when the equation connecting them is known in some form, such as

$$p=f(\theta),$$

the relation between pressure and temperature may be represented graphically by a curve, such as that shown in Fig. 110. This curve gives the pressure corresponding to any temperature when the liquid and vapour are in contact, and in stable equilibrium together. It is the curve of maximum vapour pressures, and is termed *the steam line.*[1]

In the same manner, if an enclosure be filled by a substance partly liquid and partly solid, and if the two states are in stable equilibrium together, the temperature of the mixture is that at which the solid melts under the pressure within the enclosure. This pressure is also completely determined by the temperature, and the relation connecting them may be represented graphically by a curve. This curve is the line of fusion and is called *the ice line.*

So also a solid may exist in stable equilibrium with its vapour, and we have thus a third curve which connects the temperature and pressure of a substance when existing partly in the solid state, and partly in the condition of vapour. This curve is called the *hoar-frost line* (Fig. 179).

From his experiments on the pressures of the saturated vapours of water substance above and below 0° C., Regnault[2] concluded that in passing from the vapour of the liquid to that of the solid there is no appreciable change in the vapour pressure curve, and that consequently the hoar-frost line is simply a continuation of the steam line. The

[1] The term steam line has also been applied to the curve (Fig. 114, curve C) which represents the relation between the pressure and specific volume of the saturated vapour. This need not lead to any confusion, as one connects pressure and volume, while the other connects pressure and temperature. The former is the projection on the plane p, v, and the latter the projection on the plane p, θ, of the real steam line on the characteristic surface.

[2] Regnault, *Mém. de l'Acad.*, tom. xxvi. p. 751.

difference between the vapour pressures of water and ice at 0° C. is, however, much too small to be placed in evidence by these experiments, and it was subsequently shown by Kirchhoff[1] that the steam line and the hoar-frost line are not continuous, but are distinct curves, and intersect each other at an angle. Professor James Thomson[2] then announced the theorem that the point of intersection of these curves is situated on the ice line; or, in other words, that the three curves intersect in a common point, and this was afterwards proved by M. Moutier to follow as a consequence of the principles of thermodynamics (Art. 318).

This theorem is merely the statement of the fact that there is a temperature and pressure for which the three states—solid, liquid, and

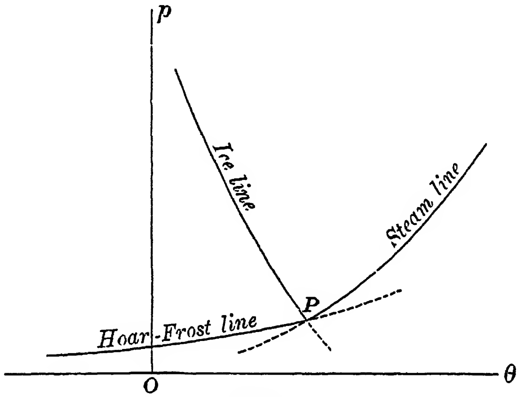

Fig. 179.

vapour—can exist simultaneously together in equilibrium. For example, there is a certain temperature and pressure at which water substance may exist partly as ice, partly as water, and partly as vapour, so that the lower part of a closed vessel containing the mixture will be filled with water in which ice floats, while the upper part is filled with saturated vapour, the pressure within the vessel being that of water vapour at the temperature of the mixture—a temperature which exceeds 0° C. by a small fraction of a degree. This temperature and pressure are those which determine the triple point, and at this temperature the pressure of the saturated vapour of the liquid is the same as that of the solid, but at no other.

The three curves shown in Fig. 179 roughly represent the two vapour pressure lines intersecting at a point P on the line of fusion. This point is the triple point for the substance to which the curves

[1] Kirchhoff, *Pogg. Ann.*, tom. ciii., 1858.
[2] J. Thomson, *Phil. Mag.* (5), vol. xlvii. p. 447.

belong, and its co-ordinates are the temperature and pressure of the triple point. In order to prove that these curves are distinct, it is only necessary to show that the tangents to them at P are inclined at different angles to the axis $O\theta$, thus denoting the three states—solid, liquid, and vapour—by the suffixes 1, 2, 3 respectively, and denoting the difference of the specific volumes by u, so that $u_{23}=(v_3-v_2)$, we have by formula (5), Art. 309, if τ be the absolute temperature of the triple point

$$\left(\frac{dp}{d\tau}\right)_{12}=\frac{L_{12}}{\tau u_{12}},\quad \left(\frac{dp}{d\tau}\right)_{23}=\frac{L_{23}}{\tau u_{23}},\quad \left(\frac{dp}{d\tau}\right)_{31}=\frac{L_{31}}{\tau u_{31}}.$$

But $dp/d\tau$ is the trigonometrical tangent of the angle which the tangent to the curve makes with the axis $O\theta$, and as the latent heats and differences of specific volume are in general different for the three changes of state, it follows that the three curves are inclined to each other at definite angles at P. Thus the difference of the trigonometrical tangents of the inclinations of the hoar-frost line and the steam line at P to the axis $O\theta$ is

$$\left(\frac{dp}{d\tau}\right)_{13}-\left(\frac{dp}{d\tau}\right)_{23}=\frac{1}{\tau}\left(\frac{L_{13}}{u_{13}}-\frac{L_{23}}{u_{23}}\right).$$

Now at the triple point, and nowhere else (see p. 677),

$$L_{13}=L_{12}+L_{23},$$

while $u_{13}=u_{12}+u_{23}$, but since u_{12} is small compared with u_{13} and u_{23} we may write $u_{13}=u_{23}$, and we obtain

$$\left(\frac{dp}{d\tau}\right)_{13}-\left(\frac{dp}{d\tau}\right)_{23}=\frac{L_{12}}{\tau u_{23}}.$$

Exercises

1. Determine the entropy ϕ and internal energy U of a mixture of liquid and saturated vapour.

[Let there be unit mass partly liquid and partly saturated vapour, and let ϕ_0 be the entropy of the mass when it is all liquid at the point A, Fig. 180. At any point M let the mass of vapour be m, while that of liquid is $1-m$, then the change of entropy in passing from A to M (considering the path ABM) is obviously[1]

$$\phi-\phi_0=\int\frac{dQ}{\tau}=\int_{\tau_0}^{\tau}\frac{s_1 d\tau}{\tau}+\frac{Lm}{\tau}\quad . \quad . \quad . \quad . \quad (1)$$

---

[1] This equation may also be deduced directly from the equation of Art. 309. For we have

$$dQ=ms_2 d\tau+(1-m)s_1 d\tau+L dm=s_1 d\tau+\tau\frac{d}{d\tau}\left(\frac{Lm}{\tau}\right),$$

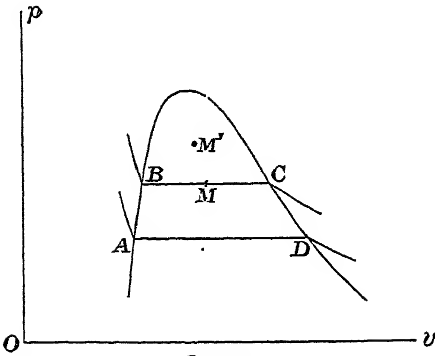

Fig. 180.

where s_1 is the specific heat of the liquid state along AB and τ the temperature of the isothermal BMC. If ϕ be supposed constant the point M will trace out an adiabatic line, and the differential equation of these lines will be

$$\frac{s_1}{\tau}+\frac{d}{d\tau}\left(\frac{\mathrm{L}m}{\tau}\right)=0 \quad . \quad (2)$$

The change of entropy of the mass in passing from the condition M to any other condition M' will consequently be

$$\phi'-\phi=\int_{\tau}^{\tau'}\frac{s_1 d\tau}{\tau}+\frac{\mathrm{L}'m'}{\tau'}-\frac{\mathrm{L}m}{\tau} \quad . \quad . \quad . \quad . \quad (3)$$

and if M and M' lie on the same adiabatic, the right-hand member of this equation is equal to zero.

To determine the internal energy we have, for the quantity of heat absorbed in passing from A to M along the path ABM,

$$\mathrm{Q}=\int_{\tau_0}^{\tau}s_1 d\tau+\mathrm{L}m \quad . \quad . \quad . \quad . \quad . \quad (4)$$

while the external work done during this transformation is

$$\mathrm{W}=\int_{\tau_0}^{\tau}p dv_1+p(v-v_1) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where v_1 is the specific volume of the liquid and v the whole volume of the mixture at M, τ the temperature at M, and τ_0 the temperature at A, the integral being taken along the line AB.

Hence

$$\mathrm{U}-\mathrm{U}_0=\mathrm{Q}-\mathrm{W}=\int_{\tau_0}^{\tau}s_1 d\tau-\int_{\tau_0}^{\tau}p dv_1+\mathrm{L}m-p(v-v_1) \quad . \quad . \quad (6)$$

But since v_1 is practically independent of the pressure we may write $dv_1=\frac{dv_1}{d\tau}d\tau$, and since $v=(1-m)v_1+mv_2$, we have

$$v-v_1=m(v_2-v_1)=m\mathrm{L}/\tau\frac{dp}{d\tau},$$

---

by the fundamental equation

$$s_2-s_1=\tau\frac{d}{d\tau}\left(\frac{\mathrm{L}}{\tau}\right).$$

Hence

$$d\phi=\frac{s_1 d\tau}{\tau}+\frac{d}{d\tau}\left(\frac{\mathrm{L}m}{\tau}\right).$$

consequently (6) becomes

$$\mathrm{U}-\mathrm{U}_0=\int_{\tau_0}^{\tau}\left(s_1-p\frac{dv_1}{d\tau}\right)d\tau+\mathrm{L}m\left(1-p/\tau\frac{dp}{d\tau}\right) \quad . \quad . \quad . \quad (7)$$

which is Clausius's expression.

If, however, we integrate by parts (5) becomes

$$\mathrm{W}=pv-p_0v_0-\int_{\tau_0}^{\tau}v_1dp \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where p_0, v_0 refer to the point A, and p, v to the point M. Hence, for the change of internal energy, we have

$$\mathrm{U}-\mathrm{U}_0=\mathrm{Q}-\mathrm{W}=\mathrm{L}m-(pv-p_0v_0)+\int_{\tau_0}^{\tau}\left(s_1+v_1\frac{dp}{d\tau}\right)d\tau \quad . \quad . \quad (9)$$

and the change of the internal energy in passing from M to any other condition M′ is

$$\mathrm{U}'-\mathrm{U}=\mathrm{L}'m'-\mathrm{L}m-(p'v'-pv)+\int_{\tau}^{\tau'}\left(s_1+v_1\frac{dp}{d\tau}\right)d\tau.$$

If M and M′ lie on the same adiabatic $\mathrm{Q}=0$, and the right-hand member of this equation represents the external work done.]

2. Prove that an adiabatic increase of temperature will diminish or increase the quantity of vapour in a mixture of liquid and vapour; or, in other words, cause condensation or vaporisation, according as the quantity

$$s_1(1-m)+s_2$$

is positive or negative, m being the mass of vapour per unit mass of the mixture.

[Taking the mass of the mixture to be unity, we have for any small transformation

$$d\mathrm{Q}=\{(1-m)s_1+ms_2\}\,d\tau+\mathrm{L}dm,$$

and since the transformation in question is adiabatic we have $d\mathrm{Q}=0$, and consequently

$$\left(\frac{dm}{d\tau}\right)_{\phi}=-\frac{1}{\mathrm{L}}\{(1-m)s_1+ms_2\}.$$

Hence, if the quantity within the bracket is positive dm and $d\tau$ have opposite signs, but if this quantity is negative dm and $d\tau$ have the same sign. That is, m increases with τ when $(1-m)s_1+ms_2$ is negative and decreases as τ increases if this quantity is positive.]

3. A mixture of liquid and vapour expands adiabatically, determine the change in the relative proportions of the liquid and vapour.

[Since the entropy is constant equation (3) of Ex. 1 gives, since s_1 is practically constant,

$$\frac{m'\mathrm{L}'}{\tau'}=\frac{\mathrm{L}m}{\tau}-s_1\log\frac{\tau'}{\tau} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now if v be the volume of the mixture at τ we have

$$v=(1-m)v_1+mv_2=v_1+m(v_2-v_1)=v_1+m\frac{\mathrm{L}}{\tau}\Big/\frac{dp}{d\tau},$$

so that

$$\frac{\mathrm{L}m}{\tau}=(v-v_1)\frac{dp}{d\tau}. \qquad \qquad (2)$$

and equation (1) becomes

$$(v'-v_1')\left(\frac{dp}{d\tau}\right)'=(v-v_1)\frac{dp}{d\tau}-s_1\log\frac{\tau'}{\tau}. \qquad \qquad (3)$$

when p and v_1 are known as functions of τ, this equation gives the new temperature τ' in terms of the new volume v', the original volume v, and the original temperature τ.

If the latent heat at τ be given, the first term of the right-hand member of (3) may be used in its original form $m\mathrm{L}/\tau$.]

4. A unit mass of saturated steam is allowed to expand adiabatically, determine when the maximum condensation has taken place.

[By Ex. 2 condensation will cease when the mass m of vapour remaining satisfies the equation

$$(1-m)s_1+ms_2=0,$$

or

$$m=\frac{s_1}{s_1-s_2}=\frac{s_1\tau}{\mathrm{L}-\tau\frac{d\mathrm{L}}{d\tau}}.$$

This result may also be obtained from equation (3) of Ex. 1 by expressing that ϕ is constant and m a maximum. In the case of steam, if

$$\mathrm{L}=800-0{\cdot}705\tau,$$

we find for the maximum condensation

$$m=\frac{\tau}{800}.]$$

5. A mixture half water and half steam at 150° C. is enclosed within a non-conducting cylinder and allowed to expand, pushing back a piston, determine what happens.

[If m be the mass of vapour present at any instant, the whole mass of the mixture being unity, then evaporation or condensation will occur according as

$$s_1+m(s_2-s_1)$$

is positive or negative. Now for water vapour we have the formula

$$\mathrm{L}=800-0{\cdot}705\tau.$$

Therefore

$$s_2-s_1=\tau\frac{d}{d\tau}\left(\frac{\mathrm{L}}{\tau}\right)=-\frac{800}{\tau},$$

so that at the temperature 150° C. we have, taking $s_1=1$, and $m=\frac{1}{2}$,

$$s_1+m(s_2-s_1)=1-\frac{400}{423}=0{\cdot}054,$$

which is a positive quantity, consequently evaporation takes place as the expansion proceeds.

This might also be seen at once from the final equation of the preceding example. For the amount of vapour present when the maximum condensation has taken place at 150° C. is $m=\frac{423}{800}={\cdot}529$, and this exceeds the quantity in our problem. Hence more vapour will form on expansion, until its quantity is $m'=\frac{\tau'}{800}$. Sub-

stituting this in equation (1), Ex. 3, we obtain an equation which gives τ' the temperature at which evaporation ceases and condensation begins. This temperature is about 120° C. Condensation then takes place, and the ratio of the vapour to the liquid will again become unity at a temperature of about 91° C.]

6. Show that when the specific heat of a saturated vapour is negative the adiabatic lines intersect the steam line (Fig. 117) passing downwards across it from right to left, and when the specific heat is positive they pass across it from left to right, their upper parts lying to the left and their lower to the right.

7. Prove that the external latent heat L_e (Art. 310) is related to the latent heat L by the equation

$$\frac{L}{L_e}=\frac{\tau}{p}\frac{dp}{d\tau}.$$

8. If the latent heat of vaporisation can be expressed in the form

$$L=a-b\tau,$$

prove that the difference of the specific heats of the liquid and the saturated vapour varies inversely as the absolute temperature.

[We have

$$s_2-s_1=\frac{dL}{d\tau}-\frac{L}{\tau}=-\frac{a}{\tau}.]$$

9. In the same case prove that the variation of the specific heat of a saturated vapour per degree of temperature is inversely proportional to the square of the absolute temperature.

[Neglecting the variations of the specific heat of the liquid, we have by Ex. 8

$$\frac{ds_2}{d\tau}=-\frac{a}{\tau^2}.]$$

10. Supposing the latent heat of vaporisation of water to be given by the formula

$$L=800-0{\cdot}705\tau,$$

calculate the temperature of inversion.

[Taking the specific heat of water to be unity we find

$$s_2=1-\frac{800}{\tau},$$

consequently the temperature of inversion ($s_2=0$) is 527° C. ; cf. Arts. 175, 213.]

11. Calculate the difference between the trigonometrical tangents of the angles which the tangents to the hoar-frost line and the steam line at the triple point make with the axis of abscissæ in the case of water substance.

[Taking the latent heat to be 80, $J=42700$, $\tau_0=273$, $u_{23}=209400$ cc., we find

$$\left(\frac{dp}{d\tau}\right)_{13}-\left(\frac{dp}{d\tau}\right)_{23}=0{\cdot}059,$$

the pressure being measured in grammes per square centimetre.]

12. Deduce the ratio of the quantities $\left(\frac{dp}{d\tau}\right)_{13}$ and $\left(\frac{dp}{d\tau}\right)_{23}$ in terms of the latent heats of fusion and evaporation. Calculate their numerical values for water substance, and compare the calculated values with the results of Regnault's experiments.

SECTION VII

CHARACTERISTIC FUNCTIONS AND THERMODYNAMIC POTENTIAL

313. Characteristic Functions—Formulæ of M. Massieu.—The two fundamental principles of thermodynamics furnish two equations connecting the three unknowns which determine the state of a body, viz.

$$dQ = dU + dW = \tau d\phi.$$

Hence, in order to determine all the coefficients relating to the substance, it is necessary to have some other equation connecting the variables which define its state. We are consequently led to expect that although these various coefficients and the state of the body cannot be determined in absence of this third equation, yet it should be possible to express them in terms of some function of the variables. This is what M. Massieu[1] has shown, and the function from which the various quantities may be derived he terms the *characteristic function* of the body. It depends upon the pair of independent variables chosen, having one form when τ and v are chosen, and another when τ and p are taken.

Thus, if we write, as in Art. 307,

$$\mathcal{J} = U - \tau\phi,$$

then the equation

$$dU = \tau d\phi - p dv. \qquad (1)$$

Variables τ and v.

may be written in the equivalent form

$$d\mathcal{J} = -\phi d\tau - p dv \qquad (2)$$

Consequently we have

$$\phi = -\frac{d\mathcal{J}}{d\tau}, \quad \text{and } p = -\frac{d\mathcal{J}}{dv}. \qquad (3)$$

while

$$U = \mathcal{J} + \tau\phi = \mathcal{J} - \tau\frac{d\mathcal{J}}{d\tau} \qquad (4)$$

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[1] F. Massieu, *Comptes Rendus*, tom lxix. pp. 858, 1057; 1869: *Journal de Physique*, tom. vi. p. 216, 1877.

Further, the specific heat at constant volume is given by the equation

$$C_v=\left(\frac{dU}{d\tau}\right)_v=-\tau\frac{d^2\mathfrak{F}}{d\tau^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

while for the difference of the specific heats we have (p. 644)

$$C_p-C_v=-\tau\left(\frac{dp}{d\tau}\right)^2\Big/\frac{dp}{dv}=\tau\left(\frac{d^2\mathfrak{F}}{d\tau dv}\right)^2\Big/\frac{d^2\mathfrak{F}}{dv^2} \quad . \quad . \quad . \quad . \quad (6)$$

therefore

$$C_p=-\tau\frac{d^2\mathfrak{F}}{d\tau^2}+\tau\left(\frac{d^2\mathfrak{F}}{d\tau dv}\right)^2\Big/\frac{d^2\mathfrak{F}}{dv^2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In like manner the isothermal elasticity and the coefficient of increase of pressure are given by the equations

$$-v\left(\frac{dp}{dv}\right)_\tau=v\frac{d^2\mathfrak{F}}{dv^2} \quad . \quad . \quad . \quad (8)$$

and

$$\frac{1}{p}\left(\frac{dp}{d\tau}\right)_v=\frac{d^2\mathfrak{F}}{d\tau dv}\Big/\frac{d\mathfrak{F}}{dv} \quad . \quad . \quad . \quad . \quad (9)$$

Thus, when the temperature and volume are taken as independent variables, all the other quantities appertaining to the condition of the substance U, p, ϕ, C_p, C_v, etc., can be expressed in terms of the function $\mathfrak{F}$, and its partial differential coefficients.

In the same way, if the pressure and temperature be chosen as independent variables, equation (1) may be thrown into the form $d(U-\tau\phi+pv)=vdp-\phi d\tau$.

Hence, if we write

$$U-\tau\phi+pv=\Phi,$$

we have

$$d\Phi=vdp-\phi d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Variables τ and p.

and consequently

$$v=\frac{d\Phi}{dp}, \quad \text{and } \phi=-\frac{d\Phi}{d\tau} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

while

$$U=\Phi+\tau\phi-pv=\Phi-\tau\frac{d\Phi}{d\tau}-p\frac{d\Phi}{dp} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

For the specific heat at constant pressure we have $dQ=dU+pdv$, or

$$C_p=\left(\frac{dU}{d\tau}\right)_p+p\left(\frac{dv}{d\tau}\right)_p=-\tau\frac{d^2\Phi}{d\tau^2} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and for the specific heat at constant volume we have

$$C_v=C_p+\tau\left(\frac{dv}{d\tau}\right)^2\Big/\frac{dv}{dp}=-\tau\frac{d^2\Phi}{d\tau^2}+\tau\left(\frac{d^2\Phi}{d\tau dp}\right)^2\Big/\frac{d^2\Phi}{dp^2} \quad . \quad . \quad (14)$$

The coefficient of expansion and the compressibility may also be expressed in terms of Φ, thus

$$\frac{1}{v}\left(\frac{dv}{d\tau}\right)_p=\frac{d^2\Phi}{d\tau dp}\Big/\frac{d\Phi}{dp} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15$$

and

$$-\frac{1}{v}\left(\frac{dv}{dp}\right)_\tau=\frac{d^2\Phi}{dp^2}\Big/\frac{d\Phi}{dp} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Hence, when the pressure and temperature are chosen as independent variables, the function Φ enables us to express all the other quantities.

Examples

1. Calculate the characteristic functions $\mathcal{J}$ and Φ in the case of a perfect gas.

[Here we have the relation $pv=R\tau$, while the internal energy is a function of the temperature only, and is given by the equation

$$dU=C_v d\tau. \quad \text{Hence } U-U_0=C_v(\tau-\tau_0) \quad . \quad . \quad . \quad (1)$$

Further, $dQ=C_v d\tau+pdv$, and therefore

$$d\phi=C_v\frac{d\tau}{\tau}+R\frac{dv}{v}.$$

Hence

$$\phi-\phi_0=C_v\log\frac{\tau}{\tau_0}+R\log\frac{v}{v_0}=(C_v+R)\log\frac{\tau}{\tau_0}-R\log\frac{p}{p_0} \quad . \quad . \quad (2)$$

and therefore

$$\mathcal{J}=U-\tau\phi=U_0-C_v\tau_0-\tau\phi_0+C_v\tau\left(1-\log\frac{\tau}{\tau_0}\right)-R\tau\log\frac{v}{v_0} \quad . \quad . \quad (3)$$

while

$$\Phi=U_0-C_v\tau_0-\tau\phi_0+\tau(C_v+R)\left(1-\log\frac{\tau}{\tau_0}\right)+R\tau\log\frac{p}{p_0} \quad . \quad . \quad (4)$$

These expressions may be verified by applying the formulæ of the preceding article. Thus

$$\frac{d\mathcal{J}}{dv}=-\frac{R\tau}{v}=-p, \quad \text{and } \frac{d\Phi}{dp}=\frac{R\tau}{p}=v, \text{ etc.}$$

In these expressions for $\mathcal{J}$ and Φ the quantity R may be replaced by k/ρ, where k is a constant, the same for all gases, and ρ is the normal density of the gas. See p. 140.]

2. Express the various coefficients of a substance in terms of the quantity $\mathcal{J}'$.

314. Condition of the Possibility of a Transformation.—When a system passes through any cycle of transformations, if dQ be the quantity of heat taken in by the system along any element of the cycle, and τ the absolute temperature of the source which yields the heat, then if the cycle be reversible, we have

$$\int\frac{dQ}{\tau}=0.$$

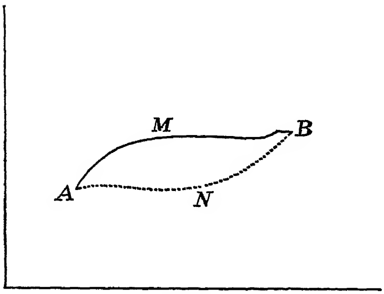

Fig. 181.

But if the conditions of reversibility be not fulfilled, we have (Art. 292)

$$\int\frac{dQ}{\tau}<0.$$

The interpretation of this is that if a system passes from a state A to

another state B, then the value of the above integral taken along any path joining A and B is greatest when the operation is reversible. In other words, $\phi_B - \phi_A$ is the same for all reversible paths joining A and B, and is greater than the integral of dQ/τ for any path between A and B which is not reversible. Thus if AMB (Fig. 181) is a reversible path, while ANB is not reversible, then considering the whole cycle ANBMA we have

$$\int_{ANB} \frac{dQ}{\tau} + \phi_A - \phi_B < 0,$$

and therefore

$$\int_{ANB} \frac{dQ}{\tau} < \phi_B - \phi_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We conclude therefore that no transformation from the state A to the state B is possible which would give the integral a value greater than $\phi_B - \phi_A$, while a transformation which would give the integral a smaller value is possible, but not reversible.

The inequality (1) is consequently the condition that a transformation from any state A to another state B may be possible. For an infinitely small change it becomes

$$dQ < \tau d\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or the quantity of heat absorbed is greatest when the operation is reversible. This is also directly obvious from the reasoning of Art. 292.

When the system is isolated $dQ = 0$, and the above inequalities (1) and (2) mean that for every possible transformation $d\phi$ must be positive; or, in other words, every possible change of the system is attended by an increase of entropy.

It follows as a corollary that in any isolated system stable equilibrium will be attained when the entropy has reached its maximum value. For in this case the entropy cannot increase, and therefore no change can take place in the system.

315. Thermodynamic Potential.—The preceding inequality which tests the possibility of a transformation may be expressed in terms of either of the characteristic functions of M. Massieu. When an elementary transformation is reversible we have

$$dQ = \tau d\phi$$
$$d\mathcal{J} = -\phi d\tau - p dv$$
$$d\Phi = v dp - \phi d\tau,$$

and when the operation does not satisfy the conditions of reversibility, we must have

$$dQ < \tau d\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$d\mathcal{J} < -\phi d\tau - p dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$d\Phi < v dp - \phi d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus by applying the inequality (1) we obtain (2) and (3) immediately. For

$$d\mathcal{J} = d(\mathrm{U} - \tau\phi) = d\mathrm{U} - \tau d\phi - \phi d\tau,$$

consequently (since $d\mathrm{Q}$ is less than $\tau d\phi$) we have

$$d\mathcal{J} < d\mathrm{U} - d\mathrm{Q} - \phi d\tau.$$

But $d\mathrm{U} - d\mathrm{Q} = -pdv$ if the only external force is a uniform normal pressure. Therefore we have

$$d\mathcal{J} < -\phi d\tau - pdv \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the same way

$$d\Phi = d(\mathrm{U} - \tau\phi + pv) = d\mathcal{J} + pdv + vdp,$$

and therefore by (2) we have

$$d\Phi < vdp - \phi d\tau \, . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Consequently (1), (2), (3) express the same condition of possibility.

We shall now consider two particular cases. In the first place, if the temperature and volume of the system remain constant, then if any transformation of the system were possible under these conditions, it must take place in such a way that we have (by 2)

$$d\mathcal{J} < 0.$$

That is, $d\mathcal{J}$ must be negative, or the transformation is possible only if it takes place in such a way as to decrease $\mathcal{J}$.

On the other hand, if the pressure and temperature remain constant, as when fusion and vaporisation are in progress, then (3) gives us

$$d\Phi < 0,$$

so that $d\Phi$ is negative, and any transformation that may be possible under these conditions [1] must be such that the function Φ decreases.

We conclude therefore that—

(α) If v and τ remain constant in any system (not isolated) the function $\mathcal{J}$ cannot increase.

(β) If p and τ remain constant in any system (not isolated) the function Φ cannot increase.

(γ) If a system be isolated the entropy cannot decrease.

From (α) we infer that when the function $\mathcal{J}$ is a minimum it is impossible for any change to take place, and consequently the system under the conditions (α) is in stable equilibrium. While from (β) we infer that the system will be in stable equilibrium when Φ is a minimum. Now in rational mechanics the equilibrium of a system is stable when

[1] J. W. Gibbs, *Trans. Connecticut Acad.*, vol. iii. pp. 108-248, 343-524; 1875-78: *Silliman's Journal*, vol. xvi. pp. 441-458; 1878: *American Journal of Arts and Sciences*, vol. xviii., 1879.

the potential energy, or the force function, is a minimum, and consequently the functions $\mathcal{J}$ and Φ here play a part corresponding to that of the force function in mechanics, and the function $\mathcal{J}$ has been accordingly named[1] by M. Duhem *the thermodynamic potential at constant volume*, while the function Φ is termed *the thermodynamic potential at constant pressure.*

316. Thermodynamic Potential of a Heterogeneous Mass.—When the mass under consideration is not homogeneous throughout, but consists of masses m_1, m_2, m_3, etc., of different qualities or in different states, the thermodynamic potential of the whole is the sum of the thermodynamic potentials of the constituents. For if U_1, U_2, U_3, etc., be the internal energies of the constituents per unit mass, then the whole internal energy is

$$U = m_1U_1 + m_2U_2 + m_3U_3 + \text{etc.},$$

and in the same way if ϕ_1, ϕ_2, ϕ_3 etc., be the entropies per unit mass of the parts, then the whole entropy is

$$\phi = m_1\phi_1 + m_2\phi_2 + m_3\phi_3 + \text{etc.}$$

Consequently we have for the whole mass, if the temperature be the same throughout,

$$\mathcal{J} = U - \tau\phi = \Sigma m_1U_1 - \tau\Sigma m_1\phi_1;$$

that is,

$$\mathcal{J} = m_1\mathcal{J}_1 + m_2\mathcal{J}_2 + m_3\mathcal{J}_3 + \text{etc.}$$

In the same way, if the pressure be the same throughout, we have $v = m_1v_1 + m_2v_2 + m_3v_3 + \text{etc.}$, and the thermodynamic potential at constant pressure is

$$\Phi = m_1\Phi_1 + m_2\Phi_2 + m_3\Phi_3 + \text{etc.}$$

Thus for a unit mass, a part m of which is in the state of saturated vapour, the remainder $1 - m$ being liquid, we have

$$\Phi = (1 - m)\Phi_1 + m\Phi_2.$$

317. Change of State.—In illustration of the preceding principles let us consider the case of a unit mass of any substance existing in two different states of aggregation. For instance, let a fraction m of it be in the state of vapour, and the remainder $1 - m$ in the liquid state. Now if a further quantity dm of the liquid becomes vapour, the pressure remaining constant, the thermodynamic potential of the liquid diminishes by an amount $\Phi_1 dm$, while that of the vapour increases by the amount $\Phi_2 dm$, where Φ_1 and Φ_2 are the thermodynamic potentials per unit mass of the liquid and vapour respectively, and

[1] P. Duhem, *Le Potentiel Thermodynamique*, Paris, 1886.

evidently remain constant under the supposed conditions. Hence the change of the thermodynamic potential of the mixture is

$$d\Phi = (\Phi_2 - \Phi_1)dm.$$

But for the possibility of any such transformation $d\Phi$ must be negative, and consequently if Φ_2 be greater than Φ_1, then dm must be negative, and condensation alone is possible, whereas if Φ_2 be less than Φ_1 dm must be positive, and vaporisation alone is possible. When Φ_2 is equal to Φ_1, either transformation is possible and reversible.

Hence, when the change of state is reversible, we have

$$\Phi_1 - \Phi_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and as Φ_1 and Φ_2 are functions of the temperature and pressure, this equation is a relation connecting the temperature and pressure of the mass when the change of state takes place in a reversible manner. Now the pressure of a mass changing state is a function of the temperature alone, and we cannot have two equations connecting p and τ, otherwise they would be completely determined, therefore the equation (1) must be the functional relation connecting the temperature and pressure during change of state; in other words, it is the equation of the steam line, the ice line, or the hoar-frost line, according to the states to which Φ_1 and Φ_2 are supposed to refer. Hence if Φ_1, Φ_2, Φ_3 refer to the solid, liquid, and gaseous states respectively, the transformation from one state to another will be reversible along any one of the lines

(Steam line)	$\Phi_2 - \Phi_3 = 0$	(1)
(Hoar-frost line)	$\Phi_3 - \Phi_1 = 0$	(2)
(Ice line)	$\Phi_1 - \Phi_2 = 0$	(3)

When the supposed transformation does not take place along one of these curves it is not reversible, and it will be impossible if it would entail an increase of Φ. We can easily examine, with regard to any one of the curves, the region in its plane for which the transformation is possible and for which impossible. Thus any curve $f(xy) = 0$ divides its plane into two regions, such that the co-ordinates of any point in one of them makes $f(xy)$ a positive quantity, while any point in the other renders it negative.

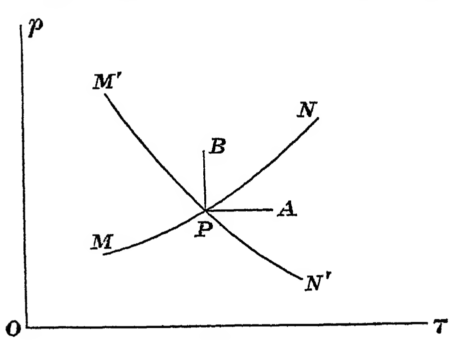

Fig. 182.

The curve itself is the line of demarcation between the two regions, and any point on it makes $f(xy)$ zero. Thus if the equation of the curve MN (Fig. 182) be

$$\Phi_1 - \Phi_2 = 0.$$

the co-ordinates of any point A not situated on the curve will not satisfy the equation of the curve, and we propose to determine whether it yields a positive or a negative value. For this purpose draw AP parallel to the axis $O\tau$, and let the co-ordinates of P be p and τ while those of A are p and $\tau + d\tau$, then the change of $\Phi_1 - \Phi_2$ in passing from P to A will be, using Massieu's formulæ,

$$\left(\frac{d\Phi_1}{d\tau} - \frac{d\Phi_2}{d\tau}\right)d\tau = (\phi_2 - \phi_1)d\tau = \frac{L}{\tau}d\tau,$$

and this is a positive quantity. Therefore A is in the positive region.

Similarly, if we take a point B whose co-ordinates are τ and $p + dp$, we have for the value of $\Phi_1 - \Phi_2$ at this point

$$\left(\frac{d\Phi_1}{dp} - \frac{d\Phi_2}{dp}\right)dp = (v_1 - v_2)dp,$$

and this will be negative if v_1 is less than v_2. Consequently we infer that if the latent heat is positive, and if the change of volume is also positive in passing from the state (1) to the state (2), then the curve $\Phi_1 - \Phi_2 = 0$ passes between the points A and B as shown in the figure, A lying in the positive region and B in the negative. If, however, the change of volume be negative, as in the fusion of ice, then the curve will not pass between A and B, but will be situated like MN′, so that the two points lie on the same side of it. In the former case increase of temperature is accompanied by increase of pressure, whereas in the latter increase of temperature is accompanied by decrease of pressure.

Let us now return to the equation

$$d\Phi = (\Phi_2 - \Phi_1)dm,$$

and consider the transformation PA (Fig. 182). In this case the value of $\Phi_2 - \Phi_1$ at A is $-L/\tau$, a negative quantity if the transformation from the state (1) to the state (2) is accompanied by absorption of heat—that is, if L is positive. In this case dm can only be positive, and we conclude that at every point on the right-hand side of the curve the only transformation possible is one in which dm is positive and entails an absorption of heat. In the same way the only trans-

formation possible to the left-hand side of the curve is one in which dm is negative and entails an evolution of heat.[1]

Similarly, if we consider the transformation PB, we find that the value of $\Phi_2 - \Phi_1$ at B is $(v_2 - v_1)dp$, and therefore if v_2 is greater than v_1 the only transformation possible in the region above the curve (dp positive) is one in which dm is negative—that is, one in which there is a decrease of volume,—whereas in the region below the curve (dp negative) the only transformation possible is one which entails an increase of volume.[2]

Thus if the pressure of a mixture of water and its saturated vapour could be increased without condensation or change of temperature, the new condition would be unstable. In this state the water cannot evaporate, but there is danger of sudden liquefaction. On the other hand, if the pressure happened to diminish without evaporation or change of temperature the vapour cannot condense, but there is danger of explosive ebullition.

Along the curve of reversible transformation $\Phi_1 - \Phi_2 = 0$, we have

$$\left(\frac{d\Phi_1}{d\tau} - \frac{d\Phi_2}{d\tau}\right)d\tau + \left(\frac{d\Phi_1}{dp} - \frac{d\Phi_2}{dp}\right)dp = 0.$$

That is

$$(\phi_2 - \phi_1)d\tau = (v_2 - v_1)dp,$$

or

$$\frac{\mathrm{L}}{\tau} = (v_2 - v_1)\frac{dp}{d\tau}.$$

318. The Triple Point.—The preceding theory may be applied at once to deduce the theorem of the triple point (Art. 312), viz. that the two vapour pressure curves (the steam line and the hoar-frost line) intersect on the line of fusion or ice line. For the equation of the steam line is

$$\Phi_2 - \Phi_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and along this the liquid and vapour are in equilibrium. The equation of the hoar-frost line is

$$\Phi_3 - \Phi_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and along this the vapour and solid are in equilibrium. Now by adding (1) and (2) together we obtain the equation of a curve which must pass through all the points in which (1) and (2) intersect each other, but the sum of (1) and (2) gives

$$\Phi_1 - \Phi_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] J. Moutier, *Bulletin de la Société Philomathique*, 6e, tom. xiii., 1876 ; 7e, toms. i. ii. iii. iv.

[2] Gustave Robin, *ibid.*, 7e, tom. iv. p. 21.

But this is the equation of the ice line, and we therefore conclude that every point of intersection of any two of these curves lies on the third.

From this it follows at once that if two of these curves coincide in any region the third must coincide with them all along their common part, or if two of them coincide completely, the three become one and the same curve, and the substance can exist in only two states. Now in the case of water the steam line and the ice line are obviously distinct, and therefore the hoar-frost line must also be a distinct curve, and cannot merge into the steam line as Regnault thought, but cuts it at an angle at the triple point.

The co-ordinates of this point obviously satisfy the equations

$$\Phi_1 = \Phi_2 = \Phi_3,$$

so that at the triple point the thermodynamic potential is the same (to a constant) for all three states.

To determine the angles at which the three curves intersect at the triple point we have, taking the steam line,

$$\left(\frac{d\Phi_2}{dp} - \frac{d\Phi_3}{dp}\right)dp + \left(\frac{d\Phi_2}{d\tau} - \frac{d\Phi_3}{d\tau}\right)d\tau = 0,$$

which by Massieu's formulæ gives at once

$$(v_2 - v_3)dp = (\phi_2 - \phi_3)d\tau\,;$$

therefore, for the inclination of the tangent to the axis of abscissæ, we have

$$\left(\frac{dp}{d\tau}\right)_{23} = \frac{\phi_2 - \phi_3}{v_2 - v_3},\quad \left(\frac{dp}{d\tau}\right)_{31} = \frac{\phi_3 - \phi_1}{v_3 - v_1},\quad \left(\frac{dp}{d\tau}\right)_{12} = \frac{\phi_1 - \phi_2}{v_1 - v_2}.$$

Hence the trigonometrical tangents of the angles are obviously connected by the relation

$$(v_2 - v_3)\left(\frac{dp}{d\tau}\right)_{23} + (v_3 - v_1)\left(\frac{dp}{d\tau}\right)_{31} + (v_1 - v_2)\left(\frac{dp}{d\tau}\right)_{12} = 0.$$

And this by the fundamental formula of Art. 309 gives

$$L_{23} + L_{31} + L_{12} = 0.$$

Hence, at the triple point, we have

$$L_{13} = L_{12} + L_{23}.$$

Writing this equation in the form

$$(v_1 - v_2)\left[\left(\frac{dp}{d\tau}\right)_{12} - \left(\frac{dp}{d\tau}\right)_{31}\right] = (v_3 - v_2)\left[\left(\frac{dp}{d\tau}\right)_{23} - \left(\frac{dp}{d\tau}\right)_{31}\right],$$

we see that if c_1, c_2, c_3 are in ascending order of magnitude, so that $c_1 - c_2$ and $c_3 - c_2$ have opposite signs, then the differences

$$\left(\frac{dp}{d\tau}\right)_{12} - \left(\frac{dp}{d\tau}\right)_{31} \text{ and } \left(\frac{dp}{d\tau}\right)_{23} - \left(\frac{dp}{d\tau}\right)_{31}$$

must have opposite signs. In other words, if the value of c_2 is intermediate between those of c_1 and c_3, then the magnitude of $\left(\frac{dp}{d\tau}\right)_{31}$ lies between those of $\left(\frac{dp}{d\tau}\right)_{12}$ and $\left(\frac{dp}{d\tau}\right)_{23}$. Hence the curve (13), which corresponds to the greatest change of volume, can be placed with reference to the other two, for the angle which the tangent to it at the triple point makes with the axis of abscissæ is intermediate in magnitude between the angles which the tangents to the other two make with the same axis. Consequently, if an ordinate be drawn cutting the three curves, the point of section with the curve (13) will lie between those with (12) and (23).

319. Applications.—The principles of thermodynamic potential have been recently applied with much success to the problems presented in the theory of solutions, dissociation, and thermoelectric phenomena.[1]

As an illustration let us take the case of a compound which dissociates into two other simple substances at a certain temperature and under constant pressure. Then if at any instant the mass of the compound present in the mixture be m_3, while the masses of the dissociated elements are m_1 and m_2, and if Φ_1, Φ_2, Φ_3 be the corresponding thermodynamic potentials per unit mass respectively, we have for the whole mass of the mixture

$$\Phi = m_1\Phi_1 + m_2\Phi_2 + m_3\Phi_3.$$

Hence, if the masses m_1, m_2, m_3 be supposed to change by amounts dm_1, dm_2, and dm_3, under the pressure p and temperature τ, we have

$$d\Phi = \Phi_1 dm_1 + \Phi_2 dm_2 + \Phi_3 dm_3 \quad . \quad . \quad . \quad . \quad (1)$$

But dm_1, dm_2, dm_3 are connected by the equation $dm_1 + dm_2 + dm_3 = 0$; so that if w_1, w_2, w_3 denote the molecular weights of the compound and its constituents respectively, we have

$$\frac{dm_1}{w_1} = \frac{dm_2}{w_2} = \frac{-dm_3}{w_1 + w_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1] A full exposition of the theory of thermodynamic potential and its applications will be found in M. Duhem's work, *Le Potentiel Thermodynamique et ses Applications*, Paris, 1886.

and consequently (1) becomes

$$(w_1+w_2)d\Phi=[(w_1+w_2)\Phi_3-w_1\Phi_1-w_2\Phi_2]dm_3.$$

Consequently, if the quantity

$$(w_1+w_2)\Phi_3-w_1\Phi_1-w_2\Phi_2$$

is positive, a change in which dm_3 is negative is alone possible, whereas if this quantity be negative the only change possible is one in which m_3 increases. If the transformation is reversible, then

$$(w_1+w_2)\Phi_3-w_1\Phi_1-w_2\Phi_2=0,$$

and this equation represents the curve of dissociation pressure. The dissociation pressure is thus a function of the temperature only, and is independent of the quantity m_3 of the original compound present, and of all such circumstances.

SECTION VIII

GEOMETRICAL REPRESENTATIONS—THERMODYNAMIC DIAGRAMS AND SURFACES

320. Plane Diagrams.—The advantage of the graphic method of representing the state of a substance by means of a point in a plane diagram, and the elegance of the method in concisely representing the whole history of a transformation, have been already illustrated in many cases. The particular case of Watt's indicator diagram (Art. 68), in which the co-ordinates of the point are taken as the pressure and volume of the substance, is that which has hitherto been most commonly employed, but evidently any pair of the five quantities p, v, τ, ϕ, U, which determine the condition of the substance, may be used for the same purpose, and it may happen that for one problem the representation may be most simply represented by one pair, while for another problem simplicity and elegance will be most easily secured by choosing another pair.

Thus when p and v are taken, as in Watt's method, the lines of constant volume (*isometrics*) and the lines of constant pressure (*isopiestics*) are systems of right lines parallel to the two axes of reference respectively, while the lines of constant temperature (*isothermals*), the lines of constant entropy (*isentropics*), and the lines of constant internal energy (*isodynamics* or *isenergics*) are each a system of curved lines of some particular form depending on the nature of the substance.

The other quantities which require to be represented on the diagram, and which depend on the nature of the transformation rather than on the nature of the substance, are the external work W performed by the body, and the quantity of heat Q supplied to it in passing from one state to another through some intermediate series of states. In the case of a pv diagram the work is represented very simply by the area enclosed by the path of the body, the ordinates at its extremities, and the axis of abscissæ, but the quantity Q is not so simply represented, as it depends not only on the area representing the work, but also on

the change of internal energy. Thus, while p, v, τ, ϕ, U are functions of the state of the body, the quantities W and Q are determined, not by the state of the body at any instant, but by the whole series of states through which the body passes from one condition to another.

On the other hand, if τ and ϕ be taken as co-ordinates, the isothermals and isentropics will be systems of right lines parallel to the axes of reference, and the isometrics, isopiestics, and isodynamics will be curves of some particular character depending on the nature of the body. The quantity Q on this diagram will be represented (like the quantity W on the pv diagram) by the area included between the path, the ordinates at its extremities, and the axis of abscissæ, for we have $dQ = \tau d\phi$, or

$$Q = \int \tau d\phi,$$

while W will depend on this area, and also on the change of internal energy experienced by the substance in passing from its initial to its final condition.

It is clear, therefore, that from general considerations there is nothing to choose between a diagram constructed with p and v as co-ordinates, and that constructed with τ and ϕ; the work and quantity of heat being represented on the former in a manner strictly analogous to that in which the heat and work are represented in the latter. This also appears from the general equations

$$dU = dQ - dW, \quad dW = pdv, \quad dQ = \tau d\phi,$$

for these are unaltered when for v, p, W we write ϕ, $-\tau$, $-Q$ respectively. Hence in our choice of co-ordinates we must be guided by considerations of convenience and simplicity in drawing the particular lines necessary to the problem in hand, as well as for the representation of W and Q. For one problem it may be most convenient to take p and v, while for another it may be much more simple[1] to take τ and ϕ, or v and ϕ, or some other pair, or perhaps some functions, of the quantities p, v, τ, ϕ, U.

When the substance passes through a complete cycle, and returns to its initial condition, the whole external work done is represented by the area of the cycle, and the heat supplied is the equivalent of this (since the internal energy has not changed) on the pv diagram, while the whole heat supplied is represented by the area of the cycle on the $\tau\phi$ diagram, and the external work done is its equivalent. For this reason the pv and the $\tau\phi$ diagrams claim special attention. The

[1] When τ and ϕ are used, Carnot's cycle takes the exceedingly simple form of a rectangle.

importance of the $\tau\phi$ diagram is also indicated by the general consideration that, although work may be transferred by mechanical contrivances (levers, etc.) from systems at lower pressures to others at higher, yet by the second law of thermodynamics the transference of heat can only take place from bodies at higher to others at lower temperatures; so that in the former case it is only necessary to ascertain the total quantity of work performed, but in the latter it is necessary to take into consideration the quantities of heat as well as the temperatures at which they are received. Hence, if in any particular problem several heat areas have to be considered, it is very important that these should be represented simply.

As an example of the use of the two systems we may take the simple case of a perfect gas. In this case we have $pv = R\tau$, and $U = C_v\tau$. Hence the isodynamic lines coincide with the isothermals whatever system of co-ordinates be chosen. If p and v be taken, then the isothermals and isentropics are given respectively by the equations $pv =$ const. and $pv^\gamma =$ const.; but if τ and ϕ be taken as co-ordinates, the curves which we require are the isometrics and isopiestics. Now, by Example 7, p. 635, we have

$$\phi = C_v \log \tau + R \log v + \text{const.} \quad . \quad . \quad . \quad . \quad (1)$$

and consequently if the volume is constant this gives for the equation of the isometrics on the $\tau\phi$ diagram

$$\phi = C_v \log \tau + \text{const.} \quad . \quad . \quad . \quad \text{(isometrics)}$$

so that they are a system of similar logarithmic curves. So also equation (1) may be written in the form

$$\phi = C_p \log \tau - R \log p + \text{const.} \quad . \quad . \quad . \quad . \quad (2)$$

and therefore the isopiestics are given by the equation

$$\phi = C_p \log \tau + \text{const.} \quad . \quad . \quad \text{(isopiestics)}$$

There are consequently a similar family of logarithmic curves. The isodynamics (as in this case they coincide with the isothermals) are a system of right lines parallel to the axis of temperature.

Examples

1. In the case of a perfect gas, if any pair of the quantities $\log v$, $\log p$, $\log \tau$, $\log U$, ϕ, be chosen as co-ordinates, show that the isothermals, isentropics, isometrics, etc., are all right lines.[1]

[1] Professor J. W. Gibbs, *Trans. Connecticut Academy of Arts and Sciences*, vol. ii. p. 325, 1871-73.

[In the case of a perfect gas we have

$$\log p + \log v - \log \tau = \text{const.}$$
$$\log U - \log \tau = \text{const.}$$
$$\phi - C_v \log \tau - R \log v = \text{const.},$$

and these equations are each linear in the quantities mentioned in question.]

2. If v and ϕ be taken as co-ordinates, show that if a series of isodynamic lines be drawn for equal infinitesimal differences of energy, then any series of right lines parallel to the axis of volume are divided into segments inversely proportional to the pressure, while any series of lines parallel to the axis of entropy are divided into segments inversely proportional to the temperature.

[This follows from the equations

$$p = -\left(\frac{dU}{dv}\right)_\phi, \quad \tau = \left(\frac{dU}{d\phi}\right)_v.]$$

321. Characteristic Surfaces.—When a plane diagram is constructed with any two variables which determine the condition of a body as co-ordinates, then every point in the plane of the diagram corresponds to a perfectly definite state of the body, and the indicator

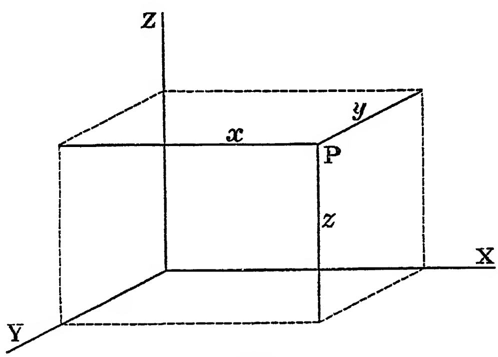

FIG. 183.

point is constrained to move along some definite curve only when the substance is forced to change its condition under some fixed law (for example, under constant temperature, or pressure, etc.). Now if any pair of the quantities p, v, τ, ϕ, U be taken as rectangular co-ordinates (or any two functions of these quantities which determine the state of the body), which for generality we shall call x and y, then at any given point on the plane diagram x and y will have given values corresponding to a definite state of the substance, so that the remaining three of the above five quantities will be perfectly determinate. Consequently, if a perpendicular be drawn to the plane of the diagram at the point xy, and if a length z be measured along it to represent any one of the other quantities, the locus of the extremity of this perpendicular in space will be a surface of some kind depending on the

nature of the substance. In other words, if any three of the quantities p, v, τ, ϕ, U be taken as the rectangular co-ordinates x, y, z of a point P (Fig. 183) in space, then as the substance passes through all possible conditions of equilibrium, the point x, y, z will describe a surface which will possess certain geometrical properties and peculiarities depending on the nature of the substance. Such a surface will consequently exhibit the characteristic properties of the substance, and may be termed a *characteristic surface.*

The particular case in which the pressure, volume, and temperature are taken as co-ordinates has been already noticed (p. 92), and the functional relation $f(p, v, \tau) = 0$, already termed the characteristic equation of the substance, is the equation of this surface. For example, in the case of a perfect gas the equation of this surface is $xy = Rz$, viz. a rectangular hyperbolic paraboloid asymptotic to the planes xz and yz. The quantities p, v, τ, being those which are directly measured in any case, are naturally the quantities which would be first chosen as co-ordinates in any geometrical representation of the properties of a substance: but it by no means follows that the surface determined by these co-ordinates will afford the most comprehensive and elegant representation of the properties of the substance. In addition we possess no general equations connecting p, v, τ, or their differential coefficients, whereas, by means of the fundamental principles of thermodynamics, we have been led to general differential equations connecting certain other quantities. For example, we have the fundamental equation

$$dU = \tau d\phi - p dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The v, ϕ, U surface.

connecting the differentials of v, ϕ, U, so that if these three quantities be chosen as co-ordinates, this equation is the differential equation of some surface of the form

$$U = f(v, \phi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

concerning which we possess at once certain valuable information. For by (1) we have

$$\left(\frac{dU}{d\phi}\right)_v = \tau, \quad \text{and} \left(\frac{dU}{dv}\right)_\phi = -p \quad . \quad . \quad . \quad . \quad . \quad (3)$$

but by (2) it follows that the direction cosines of the normal to the surface at any point are proportional to $\frac{dU}{d\phi}, \frac{dU}{dv}, -1$, and consequently by (3) it follows that the direction cosines of the normal at any point of the surface are proportional to $\tau, -p, -1$ respectively. Hence, with this surface the volume, entropy, and internal energy are given directly by the co-ordinates of a point on the surface, and the remaining pair of

quantities, viz. the pressure and temperature, are given by the direction of the normal to the surface at the same point. The whole five quantities p, v, τ, ϕ, U are thus clearly represented in an exceedingly simple manner.

Additive property.

Another advantage of the v, ϕ, U co-ordinates lies in the fact that each of them possesses the additive property. Thus in a system the volume of the whole is the sum of the volumes of the separate parts into which it may be divided; the energy of the whole is the sum of the energies of its separate parts, and similarly for the entropy. For this reason it follows that when such surfaces are constructed for different masses in the same condition, these surfaces will be similar to each other, and their linear dimensions will be simply proportional to the masses which they represent.

The surface obtained by using v, ϕ, U as co-ordinates has been brought into prominence by Professor J. Willard Gibbs,[1] and its properties will be considered briefly in the following article. At present it may be mentioned in passing that any one of the equivalent forms of the equation $dU = \tau d\phi - pdv$, viz. with the notation of Art. 307,

$$d\mathcal{J} = -\phi d\tau - pdv \quad . \quad . \quad (4)$$
$$d\mathcal{J}' = \tau d\phi + vdp \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$d\Phi = vdp - \phi d\tau \quad . \quad . \quad . \quad (6)$$

yields a surface which possesses properties characteristic of the substance, and which yields definite information as to its condition. Thus using (4), if v, τ, $\mathcal{J}$ be taken as co-ordinates, it follows that the entropy and pressure corresponding to any point are determined by the direction of the normal to the surface, and similarly in (5), when p, ϕ, $\mathcal{J}'$ are taken as co-ordinates, the direction of the normal determines τ and v, while in (6), with p, τ, Φ as co-ordinates, the volume and entropy are determined by the normal.

We are thus furnished with a considerable choice of surfaces, and that employed for any particular purpose can be selected to suit the problem in hand. Of course other surfaces may be constructed with any three functions of the quantities p, v, τ, ϕ, U as co-ordinates as may be found convenient.

322. Gibbs's Model.—The characteristic surface or thermodynamic model obtained by taking v, ϕ, U for co-ordinates has been carefully investigated by Professor J. Willard Gibbs.[1] It may be remarked at once that in constructing such a surface with regard to three mutually rectangular planes—viz. the plane of zero volume, the plane of zero

[1] J. W. Gibbs, *Trans. Connecticut Academy of Arts and Sciences*, vol. ii. p. 382, 1871-73.

entropy, and the plane of zero energy—that of zero volume alone is definite, while those of zero entropy and energy are arbitrary, for both of these quantities include an arbitrary constant. However, when the planes of reference are chosen, any point on this surface corresponds to a definite condition of the substance, and as the co-ordinates of the point represent the volume, entropy, and internal energy of the mass, it follows that any plane perpendicular to the axis of volume cuts the surface in a line of constant volume or isometric curve. Similarly the isentropics and isodynamics are the curves in which the surface is cut by planes perpendicular to the axes of entropy and energy respectively. Two systems of lines still remain for representation, viz. the isothermals and the isopiestics, and these can be very simply obtained from the conditions

$$\left(\frac{dU}{d\phi}\right)_v = \tau, \quad \left(\frac{dU}{dv}\right)_\phi = -p.$$

For if $U = f(v, \phi)$ be the equation of the surface, then if v be regarded as a constant, the relation between U and ϕ will be the equation of the

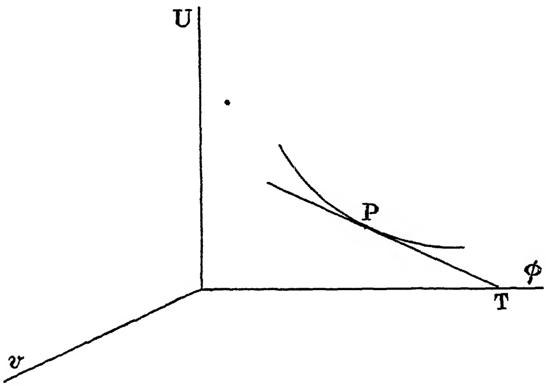

Fig. 184

isometric curve in which the surface is cut by a plane perpendicular to the axis of volume, and if a tangent line be drawn to this curve at any point, the trigonometrical tangent of the inclination of this line to the axis of entropy will be $\left(\frac{dU}{d\phi}\right)_v$. Hence if we refer to this as the *slope* of the curve at the point in question, we can say that the temperature at any point P (Fig. 184) is measured by the slope of the isometric passing through that point, and in the same way the pressure is measured by the slope of the isentropic.

The isothermal curves on the model are consequently such that if a tangent line be drawn to the surface at any point of one of them,

and in such a direction that it is perpendicular to the axis of volume, then the inclination of this line to the axis of entropy is the same at all points of the isothermal curve. The whole system of such tangent lines to any isothermal forms a system of lines, or a cylinder of rays, parallel to a line in the plane ϕU, and this cylinder obviously has ring-contact with the surface, the curve of contact being the isothermal curve. Hence we are led to Maxwell's[1] method of representing the isothermal curves on this surface, viz. place the model in the sunshine and turn it so that the sun's rays are parallel to the plane of entropy and energy, and make an angle with the axis of entropy whose tangent is proportional to the temperature. Then if we trace on the surface the boundary of light and shadow the temperature at all points of this line will be the same.

The isothermals and isopiestics.

Similarly the lines of constant pressure are found by drawing tangent lines to the surface in such a direction that they all are parallel to the plane of energy and volume, and make an angle with the axis of volume whose trigonometrical tangent measures the pressure. This system of parallel lines forms a cylinder whose line of contact with the surface is an isopiestic.

Of the various parts of a complete thermodynamic model one region consists of points which refer to the body when altogether in the solid state, another to the liquid condition, and a third to the gaseous. Besides these three parts of the surface there are other tracts which refer to the body when it is changing state and exists as a mixture of the solid and liquid, or liquid and vapour, or solid and vapour, or finally as a mixture of the three states—solid, liquid, and vapour. We shall now consider the general character of these various parts, and for the sake of brevity we shall refer to those portions which represent the solid, liquid, and vapour as the parts S, L, and V of the surface respectively, while we shall refer to that portion which represents a mixture of solid and liquid as the part SL, to that which represents the mixture of liquid and vapour as LV, to that representing the solid and vapour as SV, and to that representing a mixture of all three states as SLV.

Surface tracts.

Every point on the part S represents a definite condition of the body when altogether in the solid state, and this portion is bounded partly by a line at every point of which fusion is about to occur, and partly by a line at each point of which the substance is about to sublime. The portion S may not, however, be completely enclosed by these lines, for if anything like continuity of state exists between the liquid and solid conditions, such as Andrews proved to exist

[1] J. C. Maxwell, *Theory of Heat.*

between the liquid and gaseous, then the part S will be united to the part L of the surface by a neck or isthmus in which no discontinuity of curvature exists.

Similarly the portion L of the surface will be bounded partly by a line along which solidification is about to take place, and partly by a line at every point of which the substance is about to vaporise. These two lines do not completely enclose L, for in one region this part forms a continuation of the portion V which represents the condition of the substance when it is completely vaporised, in accordance with the experiments of Andrews. The part L is thus united to V by a neck of surface presenting no discontinuity, so that through this neck V may be regarded as a continuation of L, and it is probable that it is united to S by a similar neck, and that V is united to S in the same way.

The regions between S, L, and V are filled up by those parts of the surface (SL, LV, etc.) which represent the condition of the substance when changing state. The portion LV stretches from the fringe of L to the fringe of V, and its lines of junction with L and V are the lines already referred to, along one of which vaporisation is about to begin, and on the other of which it is completed. These two lines form what we shall call the LV *couple*, and along these lines the curvature of the surface suddenly changes so that they form lines of discontinuity of curvature on the surface regarded as a whole. For the sake of distinction we may refer to these two lines as the L line and the V line respectively of the LV couple. Similarly the part of the surface which applies to the change of state from solid to liquid is enclosed by a pair of lines, the SL couple, while the part representing sublimation is bounded by another pair, viz. the SV couple.

The node couples.

With this notation we can say that to any point A on the L line of the LV couple there is a corresponding point B on the V line of the same couple. At A vaporisation under certain conditions is about to begin, and at B it is completed. Now change of state takes place in such a way that the pressure and temperature remain the same throughout the operation, and consequently the plane which touches the part L of Gibbs's model at the point A also touches the part V at the point B, since the direction of this plane is determined by p and τ. Further, this plane touches the LV tract of the surface all along the line AB, for at every point of this line the pressure and temperature have the same values. Thus, if a plane be drawn to touch L, and also to touch V, this plane will have line-contact with LV, and the line of contact AB (Fig. 185) will be such that any point P on it represents a definite mixture of the liquid and vapour, and the point P divides

AB into segments such that P is the centre of gravity of the liquid portion of the mass placed at A and the gaseous portion placed at B.

As A moves along the L line of the LV couple B moves along the V line, and the line AB sweeps out the LV part of the surface. This part of the surface is a portion of what is called a developable surface, and may be regarded as developed in the following manner. Let a tangent plane be drawn to touch both L and V (this will be a double tangent plane), and let this plane roll on L and V, maintaining contact with both, then this plane as it passes through its consecutive positions will envelop a developable surface, viz. the surface LV. Developable sheets.

Similar remarks apply to the tracts which represent the mixtures of solid and liquid and solid and vapour. Each of these tracts (Fig. 185) is a developable surface, the tangent plane touches it along a line, and any point on one of them represents a definite mixture of two states in the manner already described.

Finally, there is a portion of the surface which possesses no curvature. This portion is a plane triangle and corresponds to the triple

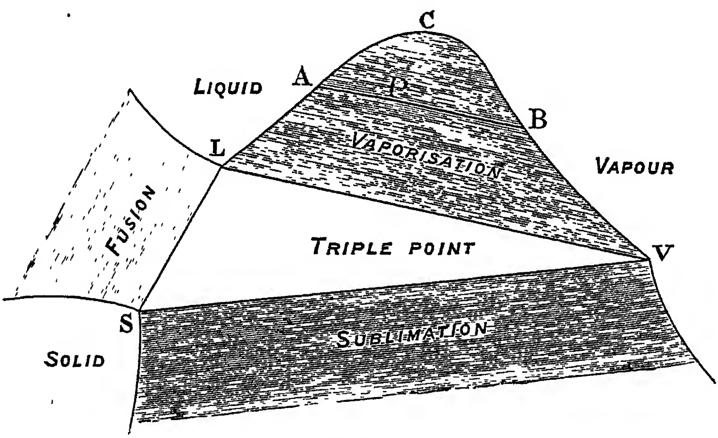

Fig. 185.

point (Art. 312), or that condition in which the substance can exist simultaneously in the solid, liquid, and gaseous states. For if a plane be drawn to touch S and also to touch L, then as this plane rolls on S and L, it is possible that in one position it may also come into contact with V. In this position the three points of contact will form a plane triangle SLV (Fig. 185), such that its vertices are points which represent conditions of the substance, at one of which it is altogether solid, at another liquid, and at the third vapour. Any point on one side of this triangle represents a definite mixture of solid and liquid,

any point on another liquid and vapour, and any point on the third solid and vapour, whereas any point within the triangle represents a definite mixture of the three states, such that the point in question is the centre of gravity of the masses of solid, liquid, and vapour placed at the corresponding vertices of the triangle.

The plane of this triangle might be supposed to start rolling on any pair of the parts S, L, V, so that if it begins to roll round a certain side of the triangle it will generate the SL developable region, starting round another edge it will develop the LV region, and round the third the SV region. However, as the two lines of the LV couple approach each other and ultimately unite so as to form a continuous curve (Andrews), it follows that as the tangent plane rolls on L and V, the points of contact A and B approach each other and ultimately coincide at a point C where the two lines of the LV couple unite. The point C (Fig. 185) is the critical point for the fluid state, and if the tangent plane be allowed to roll beyond this point it will touch the surface in a single point. The substance is here homogeneous and belongs to the neck of continuity connecting L and V.

Similar remarks apply to the SL couple and the SV couple, and if the lines of these couples unite so that each couple forms a continuous curve, then the points of junction are the critical points for the SL and SV conditions. Further, the vertices of the triangle formed by the points of contact of the triple tangent plane SLV are points at which the substance is all solid, all liquid, and all vapour respectively, and they are consequently points in which the lines of the three couples meet in pairs. Thus the S line of the SL couple and the S line of the SV couple intersect at one vertex, and the other corresponding pairs of lines intersect at the other vertices.

323. Surface of Stability.—When any thermodynamic model is constructed with three chosen co-ordinates the values of any pair may be chosen arbitrarily, but when these are given the value of the third is completely determined. It may happen that for given values of two there may be more than one corresponding value of the third, but in this case the corresponding values of the third are perfectly definite, otherwise all consideration of the surface would be illusory. The points of any such surface consequently represent all conditions of the substance which are possible and consistent with equilibrium. To fix our ideas let us suppose that the quantities p, v, τ are taken as co-ordinates, then when values of p and v are chosen corresponding to any point in the plane pv we say that there is some value (or values) of τ corresponding to equilibrium, and by erecting a perpendicular to the plane pv at the point in question, and measuring off a length which

represents this temperature, a definite point is obtained, which is a point on the surface of the model. Now when we say that to given values of p and v there is a corresponding value of τ, we merely state that there is a definite condition p, v, τ of the substance, in which it is in equilibrium, or that when the pressure and volume have values p and v then the temperature must have a certain value τ and no other. For given values of p and v and a varying value of τ the point p, v, τ is constrained to move along a right line perpendicular to the plane pv, and the point (or points) where this line meets the surface of the model is the point which represents the condition of equilibrium of the substance when its pressure is p and its volume v. If the substance were supposed to be in a state represented by any other point on this line equilibrium would not exist until the point moved to the surface.

The surface described in the preceding article, or a corresponding surface constructed with other co-ordinates, is such that the condition of the substance at every point of it is one of stable equilibrium, and it may be regarded as the surface of stability. If the condition of the substance be imagined to be represented by any point in the space inside or outside the surface, this condition will not be one of equilibrium, or if the substance happened to exist in such a state the equilibrium in this state would be unstable. Such cases of unstable equilibrium are presented in superheated globules of liquids and supersaturated solutions of salts, or over-cooled liquids and vapours, and the points representing them will not lie on the model we have constructed, but will constitute a locus outside the surface of the model similar to the theoretic part of the isothermal line conceived by Professor James Thomson (BMND, Fig. 115, p. 395). The substance at any point of this line is in unstable equilibrium, and if disturbed will rapidly change its condition till the indicator point reaches the line of stability BD. Thus we might imagine the portions S, L, V of the thermodynamic model to be parts of one continuous surface so as to be united, not by the developable sheets SL, LV, SV already described, but by portions similar to the James Thomson part of the isothermal BMND (Fig. 115). These new tracts, together with the portions S, L, V, constitute one continuous surface which exhibits no discontinuity of curvature along the line couples SL, LV, and SV; but the points of these tracts, although they represent conditions of equilibrium which may be realised under certain circumstances, are nevertheless states of unstable equilibrium.[1]

[1] The equilibrium of a system may be stable for very small disturbances and unstable for displacements of any considerable magnitude—that is, equilibrium may

Thus the portions S, L, V of the model, together with the developable sheets SL, LV, and VS, represent all possible conditions of stable equilibrium, from the very manner in which they are constructed, and all other points of space represent conditions (α) in which change is taking place, or (β) in which, if equilibrium exists, it is essentially unstable.

In the case of an isolated body, or system, thermal and mechanical equilibrium must always be established during any spontaneous changes in such a way that the point representing the state of the system moves in a plane perpendicular to the axis of energy, for since the system is isolated its energy must remain constant (the term energy here including all forms under which it appears in the system). Hence if a body, or system, be left to itself—that is, if it neither gives energy to, nor receives energy from, other bodies — then the path described by the system in passing from one condition to another must be an isodynamic line. This line may lie on the surface of the model, or it may not, but if the initial and final conditions are states of equilibrium, the extremities of the line must be situated on the surface, whereas if the whole line lies on the surface every state passed through during the transformation is one of equilibrium, and the path is an *equilibrium path.*

Isolated system.

Hence, as far as considerations of energy alone guide us, the system may pass of itself from any condition A to any other B, if A and B are on the same isodynamic line, but thermal equilibrium is always established by conduction of heat from the warmer to the colder parts of the system, and this entails an increase of entropy, so that the system cannot pass of itself from A to B, even though these points are on the same isodynamic line, unless the entropy at B is greater than the entropy at A. This consideration consequently determines the direction in which the transformation must take place, viz. in the direction of increasing entropy.

In reasoning about a system passing from one condition to another "of itself" it is all-important to attach a definite meaning to the expression, and if it is to have any just signification it should mean that during the transformation it is isolated from other systems, and consequently neither receives nor parts with energy. Now the whole energy of a system may be allocated under several heads, such as the *vis viva* of its constituent masses, the molecular energy which in part

exist and will not be broken by disturbances below a certain limit. It is the existence of such a limit that renders possible the existence of those states which we term unstable, such as superheated drops or supersaturated vapours, and it is probably determined by such magnitudes as the size of a molecule, and the distance through which molecular forces are sensible.

constitutes the sensible heat of the body, and the so-called potential energy which depends on its configuration, etc. The mode or portion of the whole energy with regard to these various constituents probably determines whether the condition of the system is one of equilibrium, and also whether this equilibrium is stable or unstable. Thus when a system is in stable equilibrium the energy is probably divided in such a way that an average is struck between kinetic and potential, as in the case of a vibrating elastic solid in which the energy is half kinetic and half potential. If, however, the energy happens to be distributed in any other manner so that the portion existing in one department is too small, while that in another is too great, as compared with this average, then the equilibrium, if it exists under such conditions, will be unstable.

Partition of the energy.

Some such partition of the energy as this would appear to exist in those unstable conditions of superheated liquid globules, etc., which are represented by the James Thomson part of the isothermal (Fig. 115). Thus at a point M the temperature is too high for the conditions of pressure and volume under which the substance exists —that is, too large a share of the energy is apportioned to the sensible heat department, and the explosion of the globule to a condition on the line BD is merely the result of the redistribution of the energy in the average manner. Similarly at N the temperature is too low, and too small a portion of the energy exists as sensible heat. At this point the vapour is over-cooled, and collapse takes place until the sensible heat has obtained its proper share.

According to this view, then, a condition of stable equilibrium of a substance is one in which the whole energy is divided into its several constituents in such a way that some average is struck in its partition, and all the states of stable equilibrium are represented by the surface of the model which consists of parts S, L, V, referring to the condition of the substance when homogeneous throughout, together with three developable tracts SL, LV, VS, and the plane triangle SLV, referring to conditions of heterogeneity in which the substance exists in two or three different states simultaneously. On this surface there is a discontinuity of curvature where S, L, V join the developable sheets, but the surface may be made continuous if the energy is apportioned among its several constituents in a different manner. The parts S, L, V can thus be joined by sheets SL, LV, VS, which form, with S, L, V, a continuous surface exhibiting no discontinuity of curvature, but the points of these new sheets correspond to a partition of energy which is inconsistent with stability.

In conclusion, we give the following example (after Professor Gibbs) in illustration of the manner in which the model may be employed in the deduction of thermodynamic formulæ. Let L and V (Fig. 186) be two corresponding points on the LV couple—at L the substance is entirely liquid, and at V it is all vapour, the change of state taking place along the line LV. Through L and V draw planes perpendicular to the axes of volume and entropy respectively. These planes will meet in a line AB parallel to the axis of energy. Further, let the tangent plane to the surface along the line LV be ALV, and let A′LV be the consecutive tangent plane. Then if LB and VC be drawn perpendicular to AB, these lines will be parallel to the axes of ϕ and v respectively. But since p and τ are represented in the manner already described (p. 684) it follows that

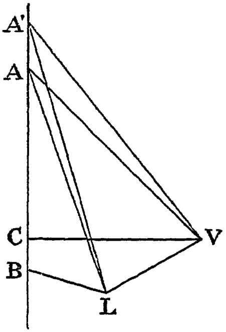

Fig. 186.

$$p=\frac{AC}{CV}, \quad \text{and } \tau=\frac{AB}{BL},$$

therefore

$$dp=\frac{AA'}{CV}, \quad \text{and } d\tau=\frac{AA'}{BL},$$

and consequently

$$\frac{dp}{d\tau}=\frac{BL}{CV}=\frac{\phi_2-\phi_1}{v_2-v_1}.$$

But $\phi_2-\phi_1$ is the change of entropy in passing from L to V, and is consequently equal to L/τ where L is the latent heat of vaporisation, so that we have the fundamental equation

$$\frac{dp}{d\tau}=\frac{L}{\tau(v_2-v_1)}.$$

SECTION IX

ON THE ABSOLUTE SCALE OF TEMPERATURE

324. Introduction. — The idea of an absolute scale of temperature, independent of the properties of any particular substance, has been briefly introduced in Art. 290, and this scale must be carefully distinguished from any other founded arbitrarily on the effects of heat on a property of some particular substance chosen for the sake of convenience. In the scale of temperature proposed in Art. 17, equal differences of temperature are measured by equal increments of volume of a fluid enclosed in a glass measuring flask, and the number representing the temperature of a body on such an instrument will depend on the nature of the particular fluid employed. Each fluid will furnish a scale possessing a zero determined by the minimum volume of the fluid, and the scales furnished by different instruments will agree neither in their zero nor throughout their length. For this reason some particular substance had to be chosen for the construction of a standard thermometer, and for this purpose a permanent gas was found to possess special advantages.

On the other hand, the system of thermometry, proposed by Lord Kelvin from thermodynamic considerations (Art. 290), is independent of the properties of any substance (and in this sense *absolute*), and we have seen that if we possessed a substance which rigorously obeyed the laws of a perfect gas,[1] then a thermometer constructed with this substance so as to measure equal changes of temperature by equal changes of volume under constant pressure, or by equal changes of pressure at constant volume, would give a scale such that the ratio of any two temperatures on it (measured from the zero of the instrument) is equal to the ratio of the quantities of heat taken in and ejected by a perfect thermodynamic engine working between these limits of temperature. Consequently, if we possessed a substance which behaved

[1] That is Boyle's law, and has R constant and γ constant, or the two specific heats constant.

as a so-called perfect gas even for some limited range of temperature, then by constructing a thermometer with this substance and graduating it within this range into degrees of any arbitrary length, the scale could be extended in both directions outside this range, and the position of the absolute zero of temperature could be determined.

Thus if air obeyed the gaseous laws rigorously between the freezing point and the boiling point of water, and if this interval of temperature be represented by 100, and if a be the expansion for 1°, then the absolute temperature of the freezing point would be $1/a$, and that of the boiling point $100 + 1/a$. But since air obeys the gaseous laws only approximately between these limits, the position of the absolute zero determined from the expansion of air in this manner is only approximate, and its true position can be determined only by observing the manner in which air deviates from these laws. When this has been determined the corresponding correction can be applied to the previous approximate scale of the air thermometer, and the instrument may be graduated according to the absolute scale.

325. First Example.—Before proceeding to the description of the experiments by which Lord Kelvin and Joule determined this correction, and reduced the indications of the air thermometer to the absolute scale, it may be advantageous to mention some general methods by which the absolute temperature τ may be deduced in terms of quantities which are capable of being determined without the aid of any previously-constructed scale of temperature. For this purpose it is evident that if we possess any thermodynamic relation, or any equation involving τ and other quantities which can be expressed in terms of p and v, then each such relation furnishes a means of estimating τ when the other quantities are known.

Thus, for example, if we take the equation of Art. 309, viz.—

$$\frac{d\tau}{\tau}=\frac{v_2-v_1}{\mathrm{L}}dp,$$

in which v_1 and v_2 are expressible in terms of p, and where L is a quantity of heat expressed in dynamical units, and requires for its estimation no previously-constructed scale of temperature, we see that τ is here expressed in terms of quantities which are capable of measurement, and which are independent of all methods of reckoning temperature. Integrating this equation we obtain

$$\log\frac{\tau}{\tau_0}=\int_{p_0}^{p}\frac{v_2-v_1}{\mathrm{L}}dp,$$

and consequently

$$\tau=\tau_{0}\int_{p_0}^{p}\frac{v_2-v_1}{L}dp.$$

This furnishes the absolute temperature corresponding to any pressure (v_1, v_2, and L being expressible in terms of p) of the mixture of liquid and saturated vapour, and the same pressure will correspond to some determinate temperature on the centigrade scale, or any other scale, and a comparison of the absolute scale with any other may be effected.

In no case, however, has the specific volume of a saturated vapour been determined with sufficient accuracy to admit of the graduation of a steam thermometer (Art. 85) in this manner, and the foregoing equation has been employed so far rather for the calculation of saturated vapour densities than as the basis of a system of absolute thermometry, and until the necessary experimental data have been obtained with much greater accuracy, the steam thermometer cannot compete with any permanent gas thermometer in furnishing an approximate estimation of temperature on the absolute scale.

In the same manner we might have employed for the expression of τ any one of the thermodynamic relations of Art. 307, or any other equation involving τ, and quantities which can be measured without reference to a scale of temperature. The foregoing is the case of the steam thermometer, and the substance exists simultaneously in two distinct states. When the state is uniform, the second thermodynamic relation may be applied, and the latent heat of isothermal expansion replaces the latent heat of change of state.

326. Second Example. — As a further illustration we shall sketch another instructive example cited by Lord Kelvin.[1] This includes the foregoing, and is the case of a substance subject to a stress which is a uniform pressure in all directions. Thus if we take p and v for independent variables in the equation

$$dQ=dU+pdv,$$

we have

$$\tau d\phi=\frac{dU}{dp}dp+\left(\frac{dU}{dv}+p\right)dv \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Consequently the equation of the adiabatic lines traced in the plane pv must be

$$\frac{dU}{dp}dp+\left(\frac{dU}{dv}+p\right)dv=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1] Art. "Heat," *Ency. Brit.* This portion of the article deals with the measurement of temperature, and is particularly vigorous.

Now if we know dU/dp and dU/dv for all values of p and v, then equation (2) yields the value of dp/dv at any point, and hence we know the direction at this point of the tangent to the adiabatic curve passing through it. By passing in this direction to the consecutive point $p+dp$, $v+dv$, the direction of the new tangent may be found in like manner, and the whole curve $\phi=$ const. may be traced. Starting out from any other point in the plane, another adiabatic curve may be traced, and the whole family of them, ϕ_1, ϕ_2, ϕ_3, etc., may be drawn in the same manner (Fig. 187).

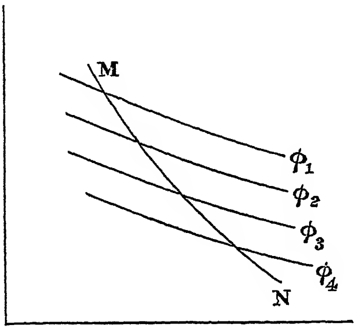

Fig. 187.

Now equation (1) gives

$$\frac{d\phi}{dp}=\frac{1}{\tau}\frac{dU}{dp}, \quad \text{and} \quad \frac{d\phi}{dv}=\frac{1}{\tau}\left(\frac{dU}{dv}+p\right);$$

consequently to determine τ we have either of the equations

$$\tau=\frac{dU}{dp}\Big/\frac{d\phi}{dp} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\tau=\left(\frac{dU}{dv}+p\right)\Big/\frac{d\phi}{dv} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence if $d\phi/dp$ and $d\phi/dv$ can be evaluated for all values of p and v, then either of the equations (3) and (4) gives τ explicitly for any particular values of p and v.

Now in tracing the adiabatic curves as above, some arbitrary constant value of ϕ was attached to each curve of the system, and the law controlling the variation of ϕ in passing from one curve of the system to another cannot be ascertained unless we know more than U as a function of p and v. The only other relation that can be found for any given substance before a scale of temperature is established is the relation connecting p and v at constant temperature, and this may be determined by means of a single thermoscope without any scale of temperature attached.

Thus if for any one arbitrary constant temperature τ_0 the isothermal relation between p and v is $p=f(v)$, then by (4) we have

$$\frac{d\phi}{dv}=\frac{1}{\tau_0}\left\{\frac{dU}{dv}+f(v)\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which dU/dv can be made a function of v alone by means of the equation $p=f(v)$. Consequently by integration of (5) we find

$$\phi=\frac{1}{\tau_0}\left\{F(v)+c\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $F(v)$ is a known function of v, and c is an arbitrary constant. Hence if the curve $p=f(v)$ be traced (MN, Fig. 187), it will cut each of the family of adiabatics previously drawn, and if the points of intersection with any pair have abscissæ v_1 and v_2, the difference of entropy on the corresponding curves will be

$$\phi_1-\phi_2=\frac{1}{\tau_0}\left\{F(v_1)-F(v_2)\right\}.$$

Thus the change of entropy in passing from one curve to another of the family of adiabatics is expressed in terms of a single arbitrary constant τ_0, and when ϕ is known in this manner the absolute temperature is furnished explicitly as a function of p and v by either of the equations (3) and (4), with the value of the constant τ_0 alone left arbitrary.

In this investigation a knowledge of the isothermal relation connecting p and v for a single temperature is required, as well as the value of $U-U_0$ for every value of p and v. This knowledge may be obtained by measurements in which no use whatever is made of any scale of temperature, and although we do not possess it for any single substance, yet less than the whole of it suffices for the construction of a thermometer graduated according to the absolute scale. For this purpose it is sufficient to know τ for all values of p and v when they are connected by any condition which may prove convenient in practice. For example, p may be kept constant, and we will then have a constant pressure absolute thermometer, or v may be maintained constant, and if we possess the information required in the above investigation under this condition, we will have a constant volume absolute thermometer.

327. The Porous Plug Experiment.—The investigation proposed by Lord Kelvin for the graduation of the constant pressure air thermometer depends in principle on the determination of the heating or cooling effect produced in a fluid when forced through a porous plug or small orifice. When a fluid is forced through a small orifice the issuing jet possesses a certain *vis viva* which gradually subsides at some distance from the orifice, and is converted into heat through fluid friction. Thus if Fig 188 represents a tube stopped at one part of its length by a diaphragm pierced by a small orifice O, and if a fluid be forced through this orifice from the side A to the side B by a piston M, which is urged forward by a pressure p, and if the fluid, as it

escapes into B, pushes another piston N before it with a pressure p'; then if M and N move with the same velocity,[1] the kinetic energy of translation of the fluid moving towards A will be the same as that moving away from it when we consider regions removed some distance from the aperture. Near the orifice, however, in the region of the

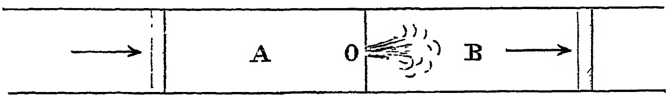

Fig. 188.

rapids, the *vis viva* of the escaping jet has not subsided, and a large part of the internal energy of the fluid exists as this *vis viva* of the mass. It might reasonably be expected, therefore, that near the orifice the temperature of the fluid would be decidedly lower than at some distance from the orifice where the *vis viva* of the issuing jet has subsided and has been converted into heat.

In an experiment made with a thermometer held near an orifice through which air was escaping under a pressure of about 8 atmos., Joule and Thomson found a depression of temperature amounting to $13^\circ{\cdot}42$ C. At a distance from the orifice, however, in the region of the tube where the motion has subsided into a uniform flow, the temperature of the stream on the side B may be either higher or lower than that on the side A, according to the nature of the escaping fluid.

Thus if U be the internal energy per unit mass on the side A, and p and v the pressure and volume, while U′, p', v' refer to the side B, then the decrease of internal energy is $U - U'$, and if no heat is supplied from without during the operation, *i.e.* if the tube and pistons are non-conductors, then $U - U'$ must be equal to the work done by the fluid. Now in the compartment B the work done by unit mass of the fluid in pushing forward the piston N is $p'v'$, and similarly, on the other side, the work done on the fluid per unit mass by the piston M is pv. Consequently we have

$$U - U' = p'v' - pv,$$

that is

$$U + pv = U' + p'v',$$

or the quantity $U + pv$ is the same before and after transit. Consequently if the product pv has not changed we must have $U = U'$, and if the internal energy depends only on the temperature, then the temperature of the stream leaving the diaphragm will be the same as that

[1] In the case of compressible fluids, this can be arranged by making the diameter of the tube on the side B larger than that on the side A.

approaching it. Hence if the temperature is found to be the same on both sides, and if the fluid obeys Boyle's law, it follows that $U = U'$, even though the pressure and specific volume vary, and hence the internal energy must be a function of the temperature only. But if the temperature changes in passing from one side to the other, then it follows that U must depend on p and v as well as on the temperature; or, in other words, Mayer's hypothesis (p. 251) will not be true. We have here, then, a test of the applicability of this hypothesis to the permanent gases which is very much more delicate than the calorimetric method adopted by Joule as explained in Art. 143. We must, however, give due allowance for deviations from Boyle's law, and the foregoing remarks are made on the supposition that this law is obeyed.

If, however, the product pv decreases as the pressure increases (as is the case up to a certain limit with all substances as shown by M. Amagat's experiments, Art. 219), then on the high pressure side of the diaphragm the internal energy will be less than on the low pressure side by an amount $U - U' = p'v' - pv$, and we would consequently expect a cooling effect, even though Mayer's hypothesis were obeyed. On the other hand, if pv increases with the pressure, as happens in the case of hydrogen and all other gases beyond a certain limit, then U' will be greater than U by an amount $pv - p'v'$, and there will be a heating effect. Hence if there is any vestige of molecular attraction in operation in the gas, mere expansion (without external work) will produce cooling, and there will be a corresponding difference of temperature on the two sides of the diaphragm, and this will be added to the cooling effect $p'v' - pv$ produced by external work in consequence of deviations from Boyle's law. On the other hand, the cooling effect arising from expansion under molecular forces will be diminished by the heating effect arising from decrease of pv under decreased pressure in the case of hydrogen and substances in a similar state.

The whole heating or cooling effect observed in any case in such an experiment will consequently be the algebraic sum of the effects arising from two different causes; but if the deviations from Boyle's law are so small as to be unobservable within the limits of experimental error, the whole effect may be attributed to the expansion under molecular forces, and will consequently be a measure of the deviation from Mayer's hypothesis.

In the experiments conducted by Joule and Lord Kelvin [1] the gas under examination was passed at a slow uniform rate through a long copper spiral tube immersed in a bath which was constantly stirred

[1] *Phil. Mag.*, 4th series, vol. iv., 1852; *Phil. Trans.*, 1853, 1854, 1862; Joule's *Scientific Papers*, vol. ii.

and kept at a uniform temperature. To the upright end, *aa* (Fig. 189), of this copper pipe a short tube of boxwood, *bb*, was secured, and in this boxwood piece a plug of cotton wool (or filaments of silk when high pressures were used) was fixed by means of two perforated brass plates shown as dotted lines at the extremities of the plug. This plug was 2·72 inches long and 1·5 inch diameter. A tin can, *d*, filled with cotton wool, was attached to the brass casting *aa*, and served to keep the water of the bath from coming in contact with the boxwood piece enclosing the plug. A thermometer was placed in the exit tube, with its bulb at a short distance above the plug, and in order to permit of the reading of the temperature this part of the tube (*ee*) was made of glass.

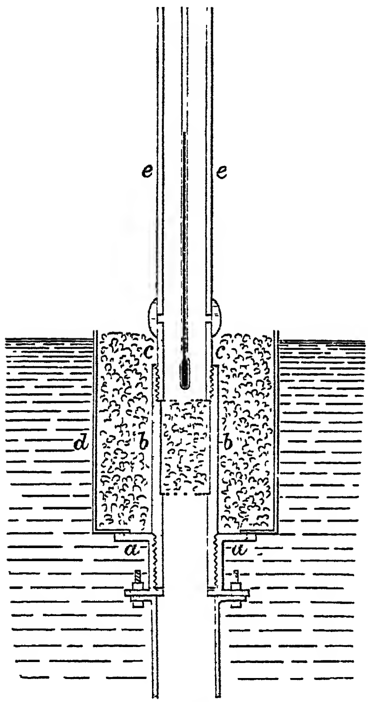

Fig. 189.

Among the difficulties met with during this investigation was the fluctuation of temperature which occurred when the stopcock was opened in order to allow the gas to flow through the tube. This arose from the initial adiabatic expansion of the gas and the compression of the air in the tube, and although this disturbance soon ceased on account of the stream of gas being in contact with the good conducting copper spiral, still further fluctuations were produced by its contact with the surface of the badly-conducting boxwood piece enclosing the plug. This effect lasted for a much longer time, and it was necessary to allow the stream to flow through the plug for a considerable period (one hour before the result could be depended on) before any observations were recorded. The cooling effect was besides exaggerated at first on account of the necessary drying of the material of the plug by the current of gas, and oscillations of temperature were caused by the intermittent action of the pump (causing adiabatic expansion or compression), so that it was very necessary to secure as uniform a flow as possible. Further, after passing through the plug, if there is any change of

temperature there will be conduction of heat through the walls of the tube, and a correction in this respect becomes necessary. This correction was determined by an experiment in which the difference of temperature between the gas and the bath was large, and it was

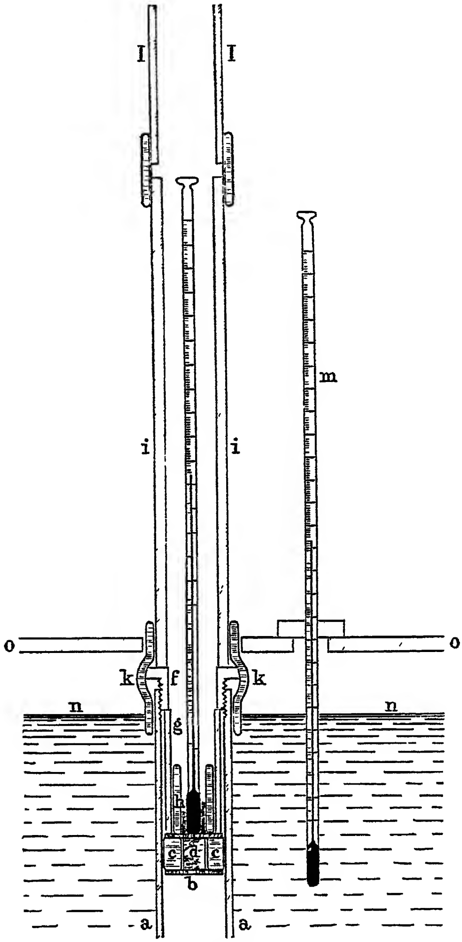

Fig. 190.

found to be directly proportional to the difference of temperature, and inversely proportional to the quantity of gas transmitted in a given time.

In the experiments at high temperatures, however, it was found necessary to increase the length of the copper spiral in order to make certain that the gas acquired the temperature of the bath. With air

and carbonic acid, which could be obtained in large quantities, the delay occasioned by the initial fluctuations of temperature caused no serious difficulty, and the nozzle depicted in Fig. 189 was considered the best. In the case of hydrogen, which could be obtained only in a limited supply, the nozzle was altered as shown in Fig. 190. The plug *d* was enclosed in a short piece of india-rubber tubing, and a cork tube, *h*, was placed within the copper tubing, in order to protect the bulb of the thermometer from the effects of a too rapid conduction of heat from the bath, and cotton wool was loosely packed round the bulb so as to distribute the current of gas as evenly as possible. The top of the glass tube *ii* was attached to a metallic tube II, which carried the gas to a reservoir in which it was preserved.

In the case of all the gases examined a thermal effect was experienced after passing through the plug, and this in the case of air, oxygen, and carbonic acid was a cooling effect. Each of these gases showed a temperature sensibly lower than the bath after passing through the plug, but in the case of hydrogen, although the first experiments appeared to give a cooling effect, a later and more accurate investigation proved that the temperature of the stream issuing from the plug was higher than that of the bath. With this gas there was therefore a heating effect, so that it stands out from the others in this respect also as it does in regard to deviations from Boyle's law. A heating effect would be expected from this gas on account of the manner in which it deviates from Boyle's law, but that this effect should more than counterbalance the cooling which must arise from residual molecular attraction, if any, or as to whether in hydrogen this latter effect should be a heating rather than a cooling, could not be predicted *a priori.*

$\delta\theta$ proportional to δp.

The thermal effect in all cases was found to be proportional to the difference of pressure on the two sides of the plug even for differences of 5 or 6 atmos., and in the case of hydrogen it amounted to a heating of $0^\circ{\cdot}039$ C. per atmosphere difference of pressure on the two sides. The law of variation of the effect with temperature was not fully determined in this case, and the foregoing number is taken as the mean of the heating effects at temperatures between 0° and 100° C.

We shall now consider how this result may be applied to the graduation of a hydrogen thermometer according to the absolute scale. For this purpose we must base the investigation on the condition which controls the experiment, viz. that the quantity $U+pv$ remains unaltered. Now the general equation $\tau\delta\phi=\delta U+p\delta v$ may be written in the form

$$\delta(U+pv)=\tau\delta\phi+v\delta p \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

and consequently, since $U+pv$ does not vary, we must have

$$\tau\delta\phi+v\delta p=0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and if p and θ (the temperature registered by an ordinary centigrade thermometer) be taken as independent variables this becomes

$$\tau\left(\frac{d\phi}{d\theta}\delta\theta+\frac{d\phi}{dp}\delta p\right)+v\delta p=0 \quad . \quad . \quad . \quad . \quad (3)$$

But by the fourth thermodynamic relation

$$\left(\frac{d\phi}{dp}\right)_\theta=-\left(\frac{dv}{d\tau}\right)_p,$$

therefore (3) becomes

$$\tau\left(\frac{d\phi}{d\theta}\right)_p\delta\theta-\tau\left(\frac{dv}{d\tau}\right)_p\delta p+v\delta p=0,$$

or

$$\tau\frac{dv}{d\tau}-v=\tau\frac{d\phi}{d\theta}\frac{\delta\theta}{\delta p};$$

now [1] in this equation

$$\tau\frac{d\phi}{d\theta}=\left(\frac{dQ}{d\theta}\right)_p=C_p,$$

therefore

$$\tau\frac{dv}{d\tau}-v=C_p\frac{\delta\theta}{\delta p} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here C_p is measured in dynamical units as a quantity of work, and its measurement does not necessarily involve the idea of a scale of temperature being merely the quantity of work required to be spent in raising a unit mass of the gas through a range indicated by two marks on a thermoscope, which if desirable might be taken as the interval of temperature between the freezing point and boiling point of water. Further, $\delta\theta/\delta p$ is the cooling (or heating) effect per unit difference of pressure on the two sides of the plug, and $\delta\theta$ may be measured in terms of the same interval of temperature as unit. Thus we now require an interval of temperature in terms of which the absolute temperature is to be expressed, and in the preceding investigation this is represented by a degree on the ordinary centigrade scale. Now for hydrogen $\delta\theta$ was found proportional to δp, and for one atmo-

[1] If there is neither heating nor cooling $\delta\theta$ is zero, and we have

$$\frac{d\tau}{\tau}=\frac{dv}{v},$$

so that

$$\log\tau=\log v+C$$

where C is a function of p alone. Consequently the characteristic equation of the substance is of the form

$$\tau=vf(p).$$

sphere difference of pressure Π we have $\delta p = -\Pi$ and $\delta\theta = 0{\cdot}039$, therefore

$$\frac{\delta\theta}{\delta p} = -\frac{0{\cdot}039}{\Pi},$$

and the equation becomes

$$\tau\frac{dv}{d\tau} - v = -\frac{0{\cdot}039}{\Pi}C_p.$$

or

$$\frac{d\tau}{\tau} = \frac{dv}{v - 0{\cdot}039C_p/\Pi} \quad . \quad . \quad (5)$$

Consequently, if we assume C_p to be constant within the range of the experiment (and its variation is undoubtedly very small) so that the effect of this variation is negligible in the small term in which C_p appears, we have by integration

$$\log\tau = \log(v - 0{\cdot}039C_p/\Pi) + \text{const.},$$

or

$$\tau = a(v - 0{\cdot}039C_p/\Pi) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where a is an arbitrary constant which depends upon the unit of temperature adopted.

If τ_0 and v_0 correspond to the freezing point of water, while τ_{100} and v_{100} correspond to the boiling point, and if this interval of temperature be represented by 100, as on the centigrade scale, then (6) gives

$$\frac{\tau_0}{\tau_{100} - \tau_0} = \frac{\tau_0}{100} = \frac{v_0 - 0{\cdot}039C_p/\Pi}{v_{100} - v_0}$$

or

$$\tau_0 = \frac{100}{\alpha}(1 - 0{\cdot}039C_p/\Pi v_0) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where α is the mean coefficient of expansion of hydrogen between the freezing and the boiling points of water.

Now v_0 is the volume of unit mass at the freezing point under the pressure p, and if V_0 be the volume per unit mass under the pressure of one atmosphere Π, then (7) may be written in the form

$$\tau_0 = \frac{100}{\alpha}\left(1 - \frac{V_0}{v_0}\cdot 039C_p/\Pi V_0\right).$$

Now Regnault found that the quantity $C_p/\Pi V_0$ for hydrogen agrees with that for air to $\frac{1}{2}$ per cent, and for air he found ΠV_0 (height of homogeneous atmosphere) = 7990, whereas the specific heat expressed in thermal units is 0·238. Hence if we take the number 427 for J the equation may be written in the form

$$\tau_0 = \frac{100}{\alpha}\left(1 + c\frac{V_0}{v_0}\right),$$

where for hydrogen $c = -\cdot 00049$, and for this gas expanding under a constant pressure of one atmosphere $\alpha = \cdot 36613$, which gives $100/\alpha = 273 \cdot 13$, therefore with $v_0 = V_0$ we find

$$\tau_0 = 273.$$

The temperature of melting ice is consequently 273° on the absolute scale when the interval between the freezing point and the boiling point of water is denoted by 100.

Numbers agreeing very closely with this were deduced from the experiments on air, and a fairly concordant figure was obtained from those on carbon dioxide. For each of these gases the thermal effect was a lowering of temperature, which, in the case of CO_2, was very decided. This cooling effect was also found to be sensibly independent of the pressure, but to vary considerably with temperature, and this variation was found to be very approximately as the inverse square of the quantity $273 + \theta$ where θ is the temperature C on the mercury thermometer, and consequently it will be sufficiently accurate to write in the small term in the denominator of (5) the cooling effect per atmo. in the form

$$A\left(\frac{273}{\tau}\right)^2,$$

and we then have

$$\frac{\delta\theta}{\delta p} = \frac{A}{\Pi}\left(\frac{\tau_0}{\tau}\right)^2,$$

where $\tau_0 = 273$. The value of A for air was found to be $0 \cdot 275$, and for carbon dioxide $1 \cdot 388$.

Returning to equation (4) we have

$$\tau\frac{dv}{d\tau} - v = C_p\frac{\delta\theta}{\delta p} = \frac{C_p A}{\Pi}\left(\frac{\tau_0}{\tau}\right)^2;$$

that is

$$\frac{d}{d\tau}\left(\frac{v}{\tau}\right) = \frac{C_p A}{\Pi}\,\frac{\tau_0^2}{\tau^4},$$

consequently

$$\frac{v}{\tau} - \frac{v_0}{\tau_0} = \int_{\tau_0}^{\tau} \frac{C_p A}{\Pi}\,\frac{\tau_0^2 d\tau}{\tau^4};$$

and therefore, if we regard C_p as constant, we have

$$\frac{v}{\tau} - \frac{v_0}{\tau_0} = \frac{C_p A \tau_0^2}{3\Pi}\left(\frac{1}{\tau^3} - \frac{1}{\tau_0^3}\right);$$

consequently we deduce at once

$$\frac{v - v_0}{v_0} = \frac{\tau - \tau_0}{\tau_0}\left\{1 + \tfrac{1}{3}A\frac{C_p}{\Pi v_0}\left(1 + \frac{\tau_0}{\tau} + \frac{\tau_0^2}{\tau^2}\right)\right\},$$

or if the interval $\tau - \tau_0$ be reckoned 100, then a denoting the coefficient of expansion between the freezing point and the boiling point of water, we have

$$\tau_0 = \frac{100}{a}\left(1 + c\frac{V_0}{v_0}\right),$$

where

$$c = \frac{C_p}{\Pi V_0}\tfrac{1}{2}A\left\{1 + \frac{\tau_0}{\tau_0+100} + \frac{\tau_0^2}{(\tau_0+100)^2}\right\} = \cdot 756A;$$

and this differs so little from

$$\tfrac{1}{2}\left\{1 + \frac{1}{(1\cdot 3663)^2}\right\}A = \cdot 769A,$$

the mean of the cooling effects at 0° and 100° C., that if this mean had been used, as was done in the case of hydrogen in absence of anything better, the effect on the result would be scarcely perceptible.

Regnault found $C_p/\Pi V_0$ greater for CO_2 than for air in the ratio 1·39 to 1 for the average of temperatures between 0° and 210°, but he also found that the specific heat of this gas varies largely with temperature, and taking the mean of its value at 0° C. and 100° C. as the proper mean in this investigation, we find that $C_p/\Pi V_0$ for this gas is 1·29 times the value of this quantity for air. This latter we have already found to be ·0126. Hence in the formula

$$\tau_0 = \frac{100}{a}\left(1 + c\frac{V_0}{v_0}\right)$$

the quantity c has the value −·00049 for hydrogen, +·0026 for air, and +·0163 for carbonic acid. The following table of results is extracted from Lord Kelvin's article :—

Name of Gas.	Expansion at One Atmo. between Freezing and Boiling Points, Regnault, a.	Proper Mean Cooling Effect per Atmo., M.	Uncorrected Estimate of Temperature of Melting Ice, $100/a$.	Correction calculated from Cooling Effect, $\frac{100}{a}\frac{C_p}{\Pi V_0}M$.	Absolute Temperature of Melting Ice, τ_0.
Hydrogen	·36613	− 0·039	273·13	− 0°·13	273
Air	·36706	+ 0°·208	272·44	+ 0°·70	273·14
Carbonic acid . . .	·37100	+ 1°·005	269·5	+ 4°·4	273·9

As the experiments on air were more trustworthy than those on hydrogen, the number 273·14 obtained from them is regarded as the most reliable approximation to the absolute temperature of melting ice.

The formula

$$\frac{v-v'}{v'}=\frac{\tau-\tau'}{\tau'}\left(1+\frac{C_p}{\Pi v'}M\right),$$

where M is the proper mean cooling effect, has been employed by Lord Kelvin to calculate the expansions of the various gases for which M is known, and the close accord between the calculated and observed values is very interesting. For air, oxygen, hydrogen, and nitrogen we have $C_p/\Pi V_0 = \cdot 0126$, so that the above formula gives the expansion between 0° and 100°,

$$a=\frac{100}{273\cdot 1}\left(1+\frac{V_0}{v_0}\cdot 0126M\right).$$

The values of M derived from Joule and Thomson's experiments are $-0\cdot 039$ for hydrogen, $+0\cdot 208$ for air, $+0\cdot 253$ for oxygen, and $+0\cdot 249$ for nitrogen.

The following numerical results are given by Lord Kelvin (Art. "Heat"):—

Name of Gas	Coeffic. of Expansion.
Hydrogen	$0\cdot 3662(1-0\cdot 00049V_0/v)$
Air	$0\cdot 3662(1+0\cdot 0026V_0/v)$
Oxygen . .	$0\cdot 3662(1+0\cdot 0032V_0/v)$
Nitrogen	$0\cdot 3662(1+0\cdot 0031V_0/v)$
Carbon dioxide . . .	$0\cdot 3662(1+0\cdot 0163V_0/v)$

For different values of V_0/v the results deduced from these formulæ are compared with those of experiment in the following table:—

[TABLE

Name of Gas	$\frac{V_0}{v}$.	Expansion (p constant) between 0° and 100° C.	
		Calculated	Observed (Regnault).
Hydrogen	0	·3662	
	1	·3660	·36613
	3	·3657	..
	3·35	·3656	·36616
	6	·3651	.
Air . . .	0	·3662	.
	1	·3672	·36706
	3	·3691	.
	3·38	·3694	·36954
	6	·3719	
Oxygen	0	·3662	
	1	·3674	.
	3	·3697	..
	6	·3732	.
Nitrogen .	0	·3662	
	1	·3673	
	3	·3696	.
	6	·3730	
Carbon dioxide . .	0	·3662	...
	1	·3721	·37099
	3	·3841	
	3·316	·3859	·38455
	6	·4019	..

Mixtures. The cooling effect was also investigated in the case of mixtures of different gases, and it was found that the cooling of the mixture on passing through the plug was not the corresponding mean of the cooling effects of the constituent gases. Thus oxygen and nitrogen taken separately showed almost the same deviations from the condition of a perfect gas, the deviation of nitrogen being slightly less than that of oxygen; but a mixture of oxygen and nitrogen appeared to deviate less than nitrogen. In the same way a mixture of CO_2 and air would be expected to show a smaller cooling effect than pure CO_2, and a larger cooling effect than air. This was found to be the case, but the cooling effect of the mixture was not that which would take place if each constituent produced its own proportion of the effect independently of the other. This evidently points to some intermolecular action between the constituents of the mixture, or to diffusion effects in passing through the plug.

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THE END

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